Intermetallic formation and oxidation in AL-AU system

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**INTERMETALLIC FORMATION AND OXIDATION IN AL-
AU SYSTEM**

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SCHOOL OF MATERIALS SCIENCE & ENGINEERING

2008

Intermetallic Formation and Oxidation in Al-Au System

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School of Materials Science & Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2008

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Abstract

Al-Au system has drawn a lot of research interests due to its wide use in microelectronic packaging technology for making interconnections, but the controversies over the interface intermetallic phases and some diffusional aspects have not been resolved. Further, no systematic investigations appear to have been reported on the effects of anneal temperature and time. The available reports lead to contradictory and ambiguous results of the phase evolution upon isothermal heat treatment. This study investigated isothermal phase transformation at 125°C, 150°C and 175°C in two Al-Au thin film structures, 0.3µm Al + 1µm Au and 1µm Al + 1µm Au. It was found that temperature didn't impact the types of intermetallic phases formed and the sequence of formation, but only affected their kinetics. The early stage of interface phase transformation in the two film structures involved the appearance of Al₂Au₅ as the first intermetallic phase followed by AlAu₄. The 1µm Al + 1µm Au structure additionally gave rise to AlAu₂ after extended annealing. The interface intermetallic phases were observed to be layered and were identified by TEM and XRD techniques. Negative ion mass SIMS depth profiling indicated that the diffusion of Au atoms into Al is more predominant than Al diffusion in the reverse direction. The kinetics of diffusion and growth in 1µm Al + 1µm Au system were found to agree with the literature reports, but in 0.3µm Al + 1µm Au system the growth rates were lower due to an apparently higher activation energy for diffusion.

Au was identified as the main diffusant in Al-Au system and a numerical model using front tracking algorithm was developed for intermetallic growth. As Al₂Au₅ was assumed to be the only intermetallic formed, this model is only valid to simulate the early stages of

intermetallic growth when Al_2Au_5 was shown to be the dominant phase. The model predicts intermetallic thicknesses very similar to those experimentally measured in $1\mu\text{m Al} + 1\mu\text{m Au}$ system, but in $0.3\mu\text{m Al} + 1\mu\text{m Au}$ case the predictions do not match with experimental results due to an incubation period exhibited in this set of samples.

The three intermetallics Al_2Au , AlAu_2 and AlAu_4 were synthesized from the elements and their crystal structure and purity were verified by XRD and thermal analysis techniques. The oxidation kinetics study of these solid samples shows that the oxidation rate constant k_p of the three intermetallics increases with increase of Au content, and the oxidation activation energy Q is similar in Al_2Au and AlAu_2 but is slightly higher for AlAu_4 . XPS surface scan for Al_2Au showed both Al oxide and the Al compound species, but only the oxidic species were detected for AlAu_2 and AlAu_4 indicating a thicker oxide layer in the latter two phases. The XPS Au peaks demonstrated the Au species for all compounds while for AlAu_4 it additionally showed two extra peaks that cannot be attributed to any known Au compound. The XPS Au 4f peaks in AlAu_4 were identified in this study for the first time. The XPS Al peaks on depth profiling for AlAu_2 and AlAu_4 showed an initial oxidized state but transformed to the Al species in each compound with increasing depth. This transformation occurred at greater depths in AlAu_4 that indicates an even thicker oxide layer in this phase. This higher tendency for AlAu_4 to oxidize has serious connotations to the wire bonding industry. These are discussed in the thesis.

Table of Contents

Acknowledgements.....	i
Abstract.....	ii
Table of Contents	iv
List of Tables.....	viii
List of Figures.....	ix
Chapter 1 Introduction	1
Chapter 2 Literature Review.....	4
2.1 Aluminum-Gold System	4
2.2 Interface Interactions in Aluminum-Gold System.....	8
2.2.1 Indirect Observation of Al-Au Intermetallic Growth.....	8
2.2.2 Growth Kinetics of Al-Au Intermetallics.....	11
2.2.3 Disagreements in Intermetallics Identification	13
2.2.4 Al-Au Intermetallics Phase Transformation Sequence	14
2.2.5 Theories of Intermetallic Formation	17
2.2.5.1 Theoretical Models in Binary System.....	17
2.2.5.2 Phenomenological Models in Al-Au System.....	24
2.3 Al-Au Intermetallic Growth in Wire Bonds.....	27
2.3.1 A Brief Introduction of Wire Bonding Technology	27
2.3.2 Interface Interactions in Al-Au Wire Bond.....	32
2.4 A Review of Oxidation	36
2.4.1 Basic Principles of Oxidation	38
2.4.2 Oxidation Characteristics of Al-Au Intermetallics	40

2.5 Formulation of Scope and Objectives.....	47
Chapter 3 Experimental Procedures	51
3.1 Material Preparation Procedures.....	51
3.1.1 Thin Film Deposition and Annealing.....	51
3.1.2 Solid Intermetallics Production	53
3.1.3 Oxidation of Solid Intermetallics.....	54
3.2 Characterization Techniques	54
3.2.1 X-ray Diffraction (XRD) for Thin Film Investigation.....	54
3.2.2 X-ray Diffraction for Solid Intermetallics	55
3.2.3 Field Emission Scanning Electron Microscopy (FESEM)	55
3.2.4 Transmission Electron Microscopy (TEM)	56
3.2.5 Secondary Ion Mass Spectrometry (SIMS)	57
3.2.6 Differential Scanning Calorimetry (DSC)	59
3.2.7 Thermogravimetry Analysis (TGA).....	60
3.2.8 X-ray Photoelectron Spectroscopy (XPS).....	61
Chapter 4 Interface Transformations in Thin Film Al-Au Diffusion Couples.....	63
4.1 0.3 μ m Al + 1 μ m Au Film Combination	63
4.2 1 μ m Al + 1 μ m Au Film Combination	83
4.3 Discussion.....	102
4.3.1 Experimental Phase Formation Sequence.....	102
4.3.2 Theoretical Prediction of Phase Formation Sequence	104
4.3.3 Dominance of Au Diffusion.....	108
4.3.4 Intermetallic Growth Kinetics	109
4.4 Conclusions.....	113
Chapter 5 Moving Boundary Model for Intermetallic Growth.....	115
5.1 Model for IMC Growth Controlled by Diffusion	115

5.2 Dimensionless Form of Equations	117
5.3 Front-Tracking Numerical Algorithm	118
5.3.1 Illustration of Algorithm	118
5.3.2 Discretization of Equations.....	119
5.4 Stability Study of Numerical Algorithm	120
5.5 Modeling Results	122
5.6 Discussion	125
5.7 Conclusions.....	127
Chapter 6 Oxidation Study of Solid Al-Au Intermetallics.....	129
6.1 Material Identifications	129
6.1.1 Thermal Identification	129
6.1.2 X-ray Diffraction Identification	132
6.2 Oxidation Kinetics	134
6.2.1 Oxidation of Pure Al	134
6.2.2 Oxidation of Al_2Au	136
6.2.3 Oxidation of AlAu_2	138
6.2.4 Oxidation of AlAu_4	139
6.2.5 Oxidation Kinetics of Solid Intermetallics	141
6.3 Surface Analysis of Oxidized Solid Intermetallics	142
6.3.1 XPS Analysis on Pure Al	143
6.3.2 XPS Analysis on Al_2Au	146
6.3.3 XPS Analysis on AlAu_2	155
6.3.4 XPS Analysis on AlAu_4	163
6.4 Discussion	171
6.4.1 Multiple Stage Oxidation.....	171
6.4.2 Oxidation Tendency of Al-Au Intermetallics.....	172

6.4.3 Chemical State Change on Surface After Oxidation.....	174
6.4.4 Chemical Reaction in Oxidation.....	176
6.5 Conclusions.....	177
Chapter 7 Relevance to Wire Bonding.....	179
7.1 Interface Transformations Study on Thin Films	179
7.2 Modeling for Intermetallic Growth.....	180
7.3 Oxidation of Common Intermetallics	180
Chapter 8 Summary	181
8.1 Interface Transformations in Thin Film Diffusion Couples.....	181
8.2 Moving Boundary Model of Intermetallic Growth.....	182
8.3 Oxidation Study of Solid Al-Au Intermetallics	183
Chapter 9 Recommendations	185
References.....	186

List of Tables

Table 2.1 Major properties of Al-Au intermetallic compounds [10]	7
Table 2.2 Typical intermetallic compounds (IMC) in some bonding systems [64]	30
Table 2.3 Wire bond shear failure modes [70]	34
Table 3.1 Specifications of the substrate Si wafer	51
Table 3.2 Major sputtering deposition conditions	53
Table 3.3 Key parameters in DSC measurements	60
Table 4.1 X-ray diffraction peaks of Au and Al	64
Table 4.2 Interplanar spacing of crystallographic planes in Au and Al	66
Table 4.3 List of interface transformations determined in the 0.3 μ m Al + 1 μ m Au samples	75
Table 4.4 Interplanar spacing of crystallographic planes in Au, AlAu ₄ and Al ₂ Au ₅	79
Table 4.5 List of interface transformations determined in the 1 μ m Al + 1 μ m Au samples	92
Table 4.6 Interplanar spacing of crystallographic planes in Au and AlAu ₄	94
Table 4.7 Interplanar spacing of crystallographic planes in AlAu ₄ , Al ₂ Au ₅ and AlAu ₂	96
Table 4.8 Interplanar spacing of crystallographic planes in Al ₂ Au ₅ and AlAu ₂	98
Table 4.9 Interdiffusion coefficients of AlAu ₂ , Al ₂ Au ₅ and AlAu ₄ [10]	105
Table 4.10 Heats of formation (ΔH°) of the Al-Au intermetallics [43]	106
Table 4.11 Comparison of atomic properties for Al and Au	109
Table 4.12 Summary of overall intermetallic growth rate constants	111
Table 5.1 Physical parameters used in modeling [10]	123
Table 6.1 Transformation temperatures for Al ₂ Au, AlAu ₂ and AlAu ₄	132
Table 6.2 List of oxidation rate constant k_p and activation energy Q values	142
Table 6.3 Summary of binding energy of Al 2p and Au 4f XPS peaks	171

List of Figures

Fig. 2.1 Al-Au phase diagram [6]	6
Fig. 2.2 Reflectivity changes at the gold surface of Al-Au thin film couples. Gold thickness = (a) 790 Å; (b) 1530 Å; (c) 3120 Å [25].....	9
Fig. 2.3 Adhesion measurement for Al-Au thin films with varying Au thicknesses [28]..	10
Fig. 2.4 Resistance change during anneal of Al-Au diffusion couple where Au:Al=2:1 [28].....	10
Fig. 2.5 Layer thickness of the five intermetallics vs. the square root of time at 400°C [29]	12
Fig. 2.6 Overall intermetallic growth at different temperatures [29].....	12
Fig. 2.7 Phase transformation diagram as suggested by Campisano [36]	15
Fig. 2.8 Al-Au phase formation sequence in Majni's study [18]	16
Fig. 2.9 Schematic of concentration profile of A atoms in the A-B diffusion couple [38]	18
Fig. 2.10 Schematic of phase 2 nucleation at interface between phase 1 and B [41].....	22
Fig. 2.11 Schematic of phase 2 nucleation between intermediate phase 1 and β [42].....	24
Fig. 2.12 Diagram showing how a time axis can be added to the phase diagram [18].....	25
Fig. 2.13 Effective heat of formation diagram and phase diagram for Al-Au system [43]	26
Fig. 2.14 Schematic illustration of ball bonding process [51]	29
Fig. 2.15 Schematic illustration of wedge bonding process [51].....	29
Fig. 2.16 Resistance change in wire bonds during annealing [69]	33
Fig. 2.17 Early growth of intermetallics in gold ball bonds [71].....	35
Fig. 2.18 Intermetallics growth during extended heat treatment [71]	35
Fig. 2.19 SEM micrographs showing (a) coexistence of Al_2Au_5 with two layers of AlAu_4 and (b) intermetallic phases in a wire bond annealed at 175°C for 200 hours [71]...	36
Fig. 2.20 Schematic illustration of a wire bond showing the location of oxidation	37
Fig. 2.21 Parabolic oxidation kinetics for Ti_3AlC_2 [87]	39
Fig. 2.22 Au 4f binding energy spectra for Al_2Au before and after 24h air exposure [91]	42

Fig. 2.23 Au 4f binding energy spectra for AlAu ₂ : (a) before 24h air exposure; (b) after 24h air exposure; (c) after reheating at 120°C for 1h [91].....	43
Fig. 2.24 Au 4f binding energy spectra for (a) Al ₂ Au and (b) AlAu ₂ after different exposure durations [90]	44
Fig. 2.25 Au 4f binding energy spectra for Al-Au alloy in moist oxidation conditions [80]	45
Fig. 2.26 Oxide thickness of Al-Au alloy and Al metal during moist oxidation [80].....	46
Fig. 2.27 Relationship between oxide thickness and the $I_{\text{AlAu}_2} / I_{\text{Al}_2\text{Au}}$ ratio [80].....	46
Fig. 2.28 Evolution of Oxygen / Aluminum concentration ratio with exposure dose [80]	47
Fig. 3.1 Experimental graph to determine Au and Al thin film sputtering deposition rate	52
Fig. 3.2 A typical crater depth profile	59
Fig. 4.1 XRD pattern for as-deposited 0.3μm Al + 1μm Au sample	64
Fig. 4.2 (a) TEM bright field micrograph of as deposited 0.3μm Al + 1μm Au sample and (b), (c) diffraction patterns of Au and Al layers.....	65
Fig. 4.3 FESEM micrograph of as deposited 0.3μm Al + 1μm Au sample	66
Fig. 4.4 XRD patterns for 0.3μm Al + 1μm Au samples annealed at three temperatures..	70
Fig. 4.5 FESEM micrographs at various sampling times showing intermetallic compounds (IMC) evolution of 0.3μm Al + 1μm Au samples at 150°C	75
Fig. 4.6 (a) TEM bright field micrograph of 0.3μm Al + 1μm Au thin film sample annealed at 150°C for 4h and (b)-(e) diffraction patterns at locations 1,2,3,4.....	78
Fig. 4.7 Negative ion mass SIMS depth profiling spectra of 0.3μm Al + 1μm Au thin film samples annealed at 150°C for various times	82
Fig. 4.8 TEM bright field micrograph of as deposited 1μm Al + 1μm Au sample.....	83
Fig. 4.9 FESEM micrograph of as deposited 1μm Al + 1μm Au sample	84
Fig. 4.10 XRD patterns for 1μm Al + 1μm Au samples annealed at three temperatures ..	87
Fig. 4.11 FESEM micrographs at various sampling times showing intermetallic compounds evolution of 1μm Al + 1μm Au samples at 150°C	91
Fig. 4.12 (a) TEM bright field micrograph of 1μm Al + 1μm Au thin film sample annealed at 150°C for 1h and (b),(c) diffraction patterns at locations 1,2	93
Fig. 4.13 (a) TEM bright field micrograph of 1μm Al + 1μm Au thin film sample annealed at 150°C for 4h and (b), (c), (d) diffraction patterns at locations 1,2,3	96

Fig. 4.14 (a) TEM bright field micrograph of $1\mu\text{m Al} + 1\mu\text{m Au}$ thin film sample annealed at 150°C for 16h and (b), (c) diffraction patterns at locations 1,2	97
Fig. 4.15 Negative ion mass SIMS depth profiling spectra of $1\mu\text{m Al} + 1\mu\text{m Au}$ thin film samples annealed at 150°C for various times	102
Fig. 4.16 Intermetallic phase transformation diagram of (a) $0.3\mu\text{m Al} + 1\mu\text{m Au}$ and (b) $1\mu\text{m Al} + 1\mu\text{m Au}$ samples in the range from 125°C to 175°C	103
Fig. 4.17 Driving forces for the formation of AlAu_2 and AlAu_4 as the second intermetallic	107
Fig. 4.18 Overall intermetallic compound growth curves for (a) $0.3\mu\text{m Al} + 1\mu\text{m Au}$ and (b) $1\mu\text{m Al} + 1\mu\text{m Au}$ thin film couples at three temperatures.....	111
Fig. 4.19 The Arrhenius plots for growth rate constant k in thin film couples	113
Fig. 5.1 Schematic illustration of modeling assumption	116
Fig. 5.2 The location of moving boundary at $j \, dT$ time level	118
Fig. 5.3 Prediction of IMC growth assuming diffusion range of $1\mu\text{m}$	124
Fig. 5.4 Prediction of IMC growth assuming diffusion range of $0.3\mu\text{m}$	125
Fig. 5.5 Illustration of the effect of dimensionless conversion.....	127
Fig. 6.1 DSC identification of Al_2Au made by arc melting.....	130
Fig. 6.2 DSC identification of AlAu_2 made by arc melting.....	131
Fig. 6.3 DSC identification of AlAu_4 made by arc melting.....	131
Fig. 6.4 XRD spectrum of Al_2Au made by arc melting.....	132
Fig. 6.5 XRD spectrum of AlAu_2 made by arc melting.....	133
Fig. 6.6 XRD spectrum of AlAu_4 made by arc melting.....	133
Fig. 6.7 Plots of (a) normalized mass gain versus oxidation time for pure Al and (b) data from (a) linearized for pure Al.....	136
Fig. 6.8 Plots of (a) normalized mass gain versus oxidation time for Al_2Au and (b) data from (a) linearized for Al_2Au	137
Fig. 6.9 Plots of (a) normalized mass gain versus oxidation time for AlAu_2 and (b) data from (a) linearized for AlAu_2	139
Fig. 6.10 Plots of (a) normalized mass gain versus oxidation time for AlAu_4 and (b) data from (a) linearized for AlAu_4	140

Fig. 6.11 Plots of $\ln k_p$ vs. $1/RT$ from which the activation energy is estimated	141
Fig. 6.12 Al 2p XPS spectra of pure Al samples oxidized up to 24 hours.....	144
Fig. 6.13 Deconvolution of Al 2p XPS spectra of pure Al samples oxidized up to 24 hours	145
Fig. 6.14 (a) Al 2p and (b) Au 4f XPS spectra of Al_2Au samples oxidized up to 24 hours	147
Fig. 6.15 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized Al_2Au	149
Fig. 6.16 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized Al_2Au ...	152
Fig. 6.17 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized Al_2Au	154
Fig. 6.18 (a) Al 2p and (b) Au 4f XPS spectra of AlAu_2 samples oxidized up to 24 hours	156
Fig. 6.19 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized AlAu_2	158
Fig. 6.20 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu_2 ...	160
Fig. 6.21 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized AlAu_2	162
Fig. 6.22 (a) Al 2p and (b) Au 4f XPS spectra of AlAu_4 samples oxidized up to 24 hours	164
Fig. 6.23 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized AlAu_4	166
Fig. 6.24 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu_4 ...	168
Fig. 6.25 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized AlAu_4	170

Chapter 1 Introduction

Wire bonding is an old technique of electronic device assembly. The basic procedure in this technology involves transfer of ultrasonic energy via the resonating bonding tool to the interface between bond wire and the bond pad to form a metallurgical connection. Bell Laboratories announced the first successful results of wire bonding application in 1957, and this technique has been extensively developed into volume production ever since. Nowadays, with the fully automatic wire bonding machines, precisely controlled bonding parameters and reproducible mechanical properties of bonding wires, bonding speed can reach 100-125 millisecond per wire interconnection including two welds and a wire loop in between, and 50 μ m pitch bonding has been achieved.

Owing to its potentially low cost, much improved yields and reliability, wire bonding has been used in all styles of microelectronic packages, from small individual chip packages to large, high-density multichip modules. The most popular applications using wire bonding are:

- Single and multi-tiered ceramic and plastic ball grid arrays (BGAs)
- Ceramic and plastic quad flat packages (QFPs)
- Chip scale packages (CSPs)
- Chip on board (COB)

The most commonly used wire materials in wire bonding technology are gold (Au) and aluminum (Al), although silver (Ag) and copper (Cu) are also used. Bonding these wire materials to various pad metallizations, predominantly Al, creates different metallurgical systems in which intermetallics form. Gold was the original material used when wire

bonding technology was first developed, and gold wire can be bonded either in the shape of a ball with a very tight spacing, or a wedge with relatively larger gap. Aluminum has become popular due to its good electrical properties and lower cost, but aluminum wire can only be wedge bonded and thus is less suitable when spacing is small.

To a large extent, the build-up of a robust wire bond depends on the metallurgical reactions alongside the interface between bonding wire and pad metallizations where intermetallic compounds formation occurs. Many researchers have unveiled that appropriate growth of intermetallics contributes to strong wire bonds, whereas excessive growth tends to deteriorate the strength and reliability of the bonds produced. There are five intermetallic compounds in the Al-Au phase diagram and some or all of them could appear in the Al-Au bonding system depending on the bonding conditions. These intermetallics grow whenever heat is required at certain stages in the assembly such as thermocompression, mould compound curing or stabilization bakes. Even at room temperature, a few monolayers of intermetallics form when the two constituent metals are brought into intimate contact.

Identification of intermetallic phases generated in Al-Au bonding system and phase evolution among the five candidate phases is crucial because this is the basis for any reliability assessment. Studies on the intermetallic growth in wire bonds show that the category of intermetallics would be different under different bonding conditions. The same happens in Al-Au thin film couples with a specific Al:Au thickness ratio upon different heat treatments. X-ray diffraction and backscattering techniques are employed to identify the phases and their thicknesses in thin film couples, but without any graphic illustrations of the structure of the resultant intermetallics, and without sufficient evidence of elemental diffusion. Meanwhile, misconception arises due to mixing of the effects of

heating temperature and time on intermetallic phase transformation as reported in some early research papers.

Associated with intermetallic compounds formation in wire bonds is often the Kirkendall voids. Kirkendall voids form because of the disparity between element fluxes entering and departing a certain region, and the consequent pile-up and condensation of vacancies resulting in reduction of contact area. On the other hand, it was found in 1970s that impurities such as Ni, Fe, Co and B can accelerate wire bond failure [1]. Subsequently, a number of other factors such as plastics, ambient atmospheres have been shown to degrade the wire bond reliability in one way or another. Therefore, it is likely that voiding and corrosion could operate concurrently depending on the experimental conditions, yet the root cause of wire bond failure may be more complex. As of today, there still exists a lack of awareness regarding bond failures induced by oxidation of Al-Au intermetallics. Until very recently, only a few papers have been published in terms of the room temperature oxidation behavior of Al-Au thin films. These papers demonstrate that, in either long-term open-air experiments or moisture accelerated measurements, oxidation of Al content in these thin films is evident and this leads to gradual but pronounced phase transformation from Al-rich phases to Au-rich phases. These latest works support the hypothesis that intermetallics in wire bonds would undergo oxidation in service, and ultimately lead to wire bond degradation, but there is no quantitative data for the measurement of Al-Au intermetallics oxidation at temperature normally encountered in wire bonding process.

Hence, the work in this thesis is aimed to examine the phase evolution and element diffusion in thin film Al-Au diffusion couples upon isothermal annealing, and oxidation behavior of selected Al-Au intermetallics.

Chapter 2 Literature Review

2.1 Aluminum-Gold System

The Al-Au system has been extensively used in microelectronic manufacturing to fabricate integrated circuits and packages [2–5]. A typical application is the Al-Au wire bonding for making interconnections between IC chip and leadframe. In this process, Au wire is thermosonically bonded to Al contacting pad on silicon die, encapsulated and cured at much higher temperature than experienced in real service. Fig. 2.1 illustrates a well-established Al-Au phase diagram constructed by Hansen and Anderko [6] based on the data of Heycock and Neville [7,8] as well as Roberts [9]. The major properties of Al-Au intermetallics are listed in Table 2.1 [10].

This system has a notorious nickname of "purple plague" which comes from the characteristic color of the Al_2Au phase [11–14], the aluminum-richest phase of the five intermetallics in the Al-Au phase diagram. Al_2Au has a homogeneity range from 32.92 to 33.92 at.% Au in the temperature range 300–400°C and possesses a *FCC* CaF_2 (C_I) type structure with lattice parameter $a = 0.601$ nm [15,16]. It is the most stable phase in the Al-Au system because of its extraordinarily high melting point (1060°C). Another intermetallic compound with a high melting point is AlAu_2 . It has three different forms: the one that is stable above 550°C possesses a MoSi_2 type structure [17] and the other two show an orthorhombically deformed MoSi_2 type substructure with a displacive superstructure [15,18,19]. Other three intermetallics, namely AlAu , Al_2Au_5 and AlAu_4 , form peritectically [18]. AlAu crystallizes in a monoclinic distorted MnP type [20], while for thin film AlAu prepared by vapour deposition in vacuum it was found to show a cubic

zinc blende type structure (B_3) with $a = 0.605$ nm [15]. Al_2Au_5 has a structure that is possibly a distorted form of the BCC ($D 8_2$) structure of γ -brass, and some researchers suggested that Al_2Au_5 could be Al_3Au_8 instead [21,22]. AlAu_4 has both high and low temperature polymorphic forms labeled as β and β' [15]. The β' phase has a cubic structure ($a = 0.692$ nm) similar to cubic β -Mn (A_{13} type) and is stable between room temperature and 500°C [23]. The β phase is of BCC (A_2) type structure with $a = 0.324$ nm. Considerable thermal hysteresis is observed in the $\beta \leftrightarrow \beta'$ transformation and, on cooling, the β phase is stable till about 400°C . M. H. Francombe *et al* [24] found the orientation relationship between these two phases during mutual transformation as follows:

$$(001)_{\beta'} // (02\bar{1})_{\beta}$$

$$[100]_{\beta'} // [012]_{\beta}$$

$$[010]_{\beta'} // [100]_{\beta}$$

Fig. 2.1 Al-Au phase diagram [6]

Table 2.1 Major properties of Al-Au intermetallic compounds [10]

Phase	Crystal Structure (unit cell, Å)	Composition at.% Au	Vicker's Hardness (5 Kg)	Specific Resistance (Ohm-cm)	Coefficient of Linear Expansion (10^{-5})	Color of the Phase	Heats of Formation at 400K (cal ±500)
Au	FCC, a=4.08	84 – 100	60 – 90	2.3	1.42	Gold	
Au ₄ Al	Cubic β-Mn (A13) (Low-temp. <500°C), a=6.92	80 – 81.2	334	37.5	1.2	Tan	
	BCC (A2) (High-temp. 500°C), a=3.24						
Au ₅ Al ₂	Distorted BCC (D8 ₂) Isotypic with γ-brass	72.7	271	25.5	1.4	Tan	
Au ₂ Al	MoSi ₂ -type (>550°C) Orthorhombically deformed MoSi ₂ -type with a displacive superstructure	65 – 66.8	130	13.1	1.3	Tan	-8300
AuAl	(Thin film) Zinc blende (B3), a=6.05 Monoclinic distorted MnP type	50	249	12.4	1.2	White	-9200
AuAl ₂	CaF ₂ (C1) type, a=6.01	32.33 – 33.92	263	7.9	0.94	Purple	-10100
Al	FCC, a=4.05	0 – 0.6	20 – 50	3.2	2.3	Lustrous	

2.2 Interface Interactions in Aluminum-Gold System

The conventional way to study the nucleation and growth of intermetallic compounds is to make thin film diffusion couples of interest and anneal to start the reaction. In early days, the reaction within Al-Au thin film was investigated by monitoring the optical reflectivity, resistance change or adhesion properties. These observations were followed by investigations using techniques with higher sensitivity and resolution such as electron and X-ray diffraction and backscattering measurements.

2.2.1 Indirect Observation of Al-Au Intermetallic Growth

In the optical reflectivity measurements, changes of reflectivity on the surface of the Al-Au diffusion couple on glass slides during anneal were recorded. A typical reflectivity measurement made by C. Weaver on the gold surface on top of excessive aluminum underlayer [25] is reproduced as Fig. 2.2. The reflectivity is plotted as a function of t/d^2 , where t is the time and d is the thickness of the gold film. The reflectivity drops to a lower steady value which is characteristic of AlAu_2 , and the abrupt break in the reflectivity curve suggests a sharply defined front of this phase advancing through the gold film to the surface. Measurement on the aluminum side gave a similar result. The motion of phase boundary was recorded to follow the relation $X^2 = Dt$ [26], where X is the film thickness, D the diffusion coefficient and t the time for phase boundary to move from the Al-Au interface to the surface, and thus the diffusion coefficients of Al in Au and Au in Al at 84°C were calculated to be $10.1 \times 10^{-19} \text{ m}^2/\text{sec}$ and $2.0 \times 10^{-19} \text{ m}^2/\text{sec}$ respectively.

Fig. 2.2 Reflectivity changes at the gold surface of Al-Au thin film couples. Gold thickness = (a) 790 Å; (b) 1530 Å; (c) 3120 Å [25]

Optical technique was also used by Takei and Francombe [27] to measure the interfacial strains in thin film samples during phase transformation due to the structural differences among Al-Au intermetallics. It was found that there was an overall increase of strain during phase transformation, but from Al_2Au_5 to AlAu_2 , there was a stress relief process, the nature of which was not clearly understood.

Weaver and Parkinson suggested using adhesion or electrical resistance as the indicator to investigate the interdiffusion reaction in Al-Au thin films [28]. In their experiments, Au films of various thicknesses were deposited on glass slide as the underlayer, on which Al was coated. The diffusion couples were annealed at 50°C and it was found that the adhesion of the thin film to the glass slide increased tremendously after a particular annealing time as a function of the Au film thickness (Fig. 2.3). This was concomitant with the change of color on the Au surface from gold to gray as viewed through the glass slide. The monitoring of electrical resistance of a diffusion couple with Au:Al thickness

ratio of 2:1 showed a typical resistance change as shown in Fig. 2.4. It can be seen that the resistance rises steadily to a maximum and then decreases slightly to a final steady state. The peak was interpreted as the end point of the reaction, and the subsequent slump as the ordering of the AlAu_2 phase. The diffusion coefficient of Al in Au at 76°C was calculated to be $5.85 \times 10^{-19} \text{ m}^2/\text{sec}$ when the final constant resistance was taken to be the end point of reaction, or $1.15 \times 10^{-19} \text{ m}^2/\text{sec}$ if the peak resistance was taken as the end point. A clear disparity was caused if different criteria for end of reaction were used.

Fig. 2.3 Adhesion measurement for Al-Au thin films with varying Au thicknesses [28]

Fig. 2.4 Resistance change during anneal of Al-Au diffusion couple where Au:Al=2:1 [28]

2.2.2 Growth Kinetics of Al-Au Intermetallics

Philofsky [29] investigated the intermetallic compounds formation in bulk Al-Au diffusion couples by joining 25 mil diameter Au and Al wires using butt-welding and then annealing the joint between 200-460°C in a forming gas atmosphere of 5% H₂ and 95% N₂. All the five intermetallics in Al-Au system were observed but not exactly in every specimen. Al₂Au and Al₂Au₅ were found to nucleate immediately and follow a parabolic law in growth. The purple phase Al₂Au showed a slow growth rate and was found only in minute quantities. Kirkendall voids were observed in this phase and, in some cases, could condense to develop a continuous line to deteriorate the strength of the joint. Al₂Au₅ grew at the fastest rate such that it was dominant regardless of time and temperature. Voiding would occur in this phase and cracks could propagate along the void line. Subsequently, AlAu₂, AlAu and AlAu₄ nucleated and coalesced one by one to form a single continuous phase. There seemed to exist an interaction of formation and growth among these phases. For example, the growth rate of Al₂Au was apparently lowered by the nucleation of AlAu₂ and, when AlAu was formed, Al₂Au even began to shrink. Fig. 2.5 illustrates the growth curves for each intermetallic at 400°C. However, the overall increase of intermetallic compound thickness at different temperatures collectively showed parabolic mechanism as illustrated in Fig. 2.6. The growth rate constants at various temperatures could be fitted by an Arrhenius relationship as follows:

$$k = 5.2 \times 10^{-4} \times \exp\left(\frac{-15900}{RT}\right) \text{ cm}^2 / \text{sec}$$

Fig. 2.5 Layer thickness of the five intermetallics vs. the square root of time at 400°C [29]

Fig. 2.6 Overall intermetallic growth at different temperatures [29]

2.2.3 Disagreements in Intermetallics Identification

According to Al-Au phase diagram, five intermetallic compounds could be formed in thin film diffusion couples since there is a significant concentration gradient across the interface. It is, however, difficult to predict the sequence of phase formation simply based on phase diagram. This is mainly because phase diagram represents an equilibrium state, while such equilibrium doesn't exist in thin film diffusion process. The phases formed and the formation sequence seem to depend on the quantity of Al and Au rather than the stability of intermetallic compounds themselves [30,31]. Therefore, many researchers have reported different results of phase formation in Al-Au system due to different Au/Al contents and sample preparation procedures they performed.

Weaver and Brown [28] reported the presence of AlAu_2 and Au without noticeable existence of Al_2Au when the Au:Al atomic ratio was greater than 2. On the contrary, when there was an excessive Al content with $\text{Al:Al} > 2$, the thin film couples consisted of Al_2Au and Al with absence of AlAu_2 . When Al:Au ratio was nearly unity, both AlAu_2 and Al_2Au were observed. Fouracre [32] observed in an in-situ transmission electron microscopy (TEM) study the movement of a well defined phase boundary of the emerging new phase from a thick bimetallic area consisting of both aluminum and gold to the thin electron transparent aluminum region. The phase boundary motion took place rapidly through crystallites but was retarded by the grain boundaries in aluminum region, and AlAu_2 was identified by electron diffraction as the only phase present. Exclusive formation of AlAu_2 was also observed by Loisel and Arakawa [33] using the attenuated total reflection method in thin film Al-Au diffusion couples heat treated in the 64-80°C temperature range. Francombe *et al* [24] made a number of diffusion couples according to the stoichiometric atomic ratio of the intermetallics and detected a series of Al-Au

intermetallics such as AlAu, Al₂Au₅, AlAu₂ and AlAu₄ in thin films and bulk structures using both electron and X-ray diffraction techniques. Vandenberg *et al* [34] reported, apart from the common intermetallic compounds, the observation of α -Au(Al) solid solution in Al-Au couples heated between 260-450°C. More recently, Eakins *et al* [35] made two sets of samples, Au films deposited on electron transparent Al disc and vice versa, for in-situ TEM investigation for the effects of oxide on Al-Au intermetallic growth. They found, upon increasing temperature during observation, majority of Al₂Au was in combination with AlAu and AlAu₂ in the Al disc, whereas Al₂Au₅, AlAu₂ and AlAu₄ were in the Au disc.

Obviously, there exists a significant disagreement in identifying Al-Au intermetallics in various experiments, leading to the uncertainty in determining the Al-Au intermetallics formation in any specific diffusion couples. Moreover, not much work has been done to demonstrate the microstructure and morphology of the intermetallics. Even micrographic illustrations of the intermetallics are rare.

2.2.4 Al-Au Intermetallics Phase Transformation Sequence

Attempts were also made to track the phase transformation sequence in Al-Au system upon thermal treatment. Earliest results came from Campisano and coworkers [36] whose primary attention was directed to cases where Al was plentiful, e.g. 3000 Å Al film deposited onto 1000 Å Au. In general, Al₂Au₅ was easily detected in the as-deposited samples, while AlAu₂ would appear after storage at room temperature for several hours. On increasing the temperature or annealing time, AlAu₂ became dominant. With unreacted Al present, AlAu₂ would remain stable only up to 150°C for 2 hours. Subsequent heating produced Al₂Au at the Al/AlAu₂ interface and the advancement of

Al_2Au through AlAu_2 . The end point was the coexistence of Al_2Au with remaining Al. On the other hand, when Au was abundant, such as 400 Å Al film deposited onto 1600 Å Au, AlAu_2 would be replaced by Al_2Au_5 as the dominant phase, and the end point in this case was the appearance of AlAu_4 in the presence of unreacted Au. Within the resolution limits of the backscattering technique used, no evidence was found for the presence of AlAu phase. Fig. 2.7 demonstrates the aforementioned phase transformation sequence. Campisano also specified the rate constants of growth for AlAu_2 and Al_2Au phases as follows:

$$k = 1.4 \times \exp\left(\frac{-1.03}{kT}\right) \text{ cm}^2 / \text{sec} \quad \text{for AlAu}_2$$

$$k = 2.0 \times \exp\left(\frac{-1.20}{kT}\right) \text{ cm}^2 / \text{sec} \quad \text{for Al}_2\text{Au}$$

Fig. 2.7 Phase transformation diagram as suggested by Campisano [36]

A more detailed and comprehensive study to thoroughly track the phase transformation

sequence in Al-Au system was Majni's investigations to react Al and Au thin films of various thicknesses [18]. In his study, Au and Al films were deposited consecutively with the Au:Al atomic ratios of approximately 1:2, 1:1, 2:1, 5:2 and 4:1 respectively. After deposition, these samples were annealed in the temperature range of 80-600°C. No appreciable intermixing between the Au and Al films was detected immediately after the deposition, but initial intermetallic phase formation was observed even at room temperature and progressed with time. A few months later, thousands of angstroms of intermetallic compound was formed and was identified as Al_2Au_5 in combination with unreacted Au or Al. Most samples demonstrated the growth of AlAu_2 after annealing at 80°C for 15 min. Further annealing at higher temperatures, however, produced different phase formation sequence depending upon the relative quantities of Al and Au as given in Fig. 2.8.

Fig. 2.8 Al-Au phase formation sequence in Majni's study [18]

Campisano and Majni generalized the intermetallic formation sequence, but did not separate the effects of annealing temperature and time. It is, therefore, not straightforward to determine whether one intermetallic phase is formed due to higher temperature or longer annealing time. It is also ambiguous to deduce the formation sequence in isothermal annealing based on these diagrams where the temperature is not fixed.

2.2.5 Theories of Intermetallic Formation

2.2.5.1 Theoretical Models in Binary System

Prediction of the sequence of intermetallic compound formation is rather difficult. A hypothetical explanation, paraphrased as the “first phase, fast phase” theory, was proposed purely in the context of kinetics [37]. This hypothesizes that all the compounds are formed at the same time but the appearance of one or another depends upon their growth rates. The first phase to appear usually has the highest diffusivity and, hence, grows fast, while the growth of the other phases with lower diffusivities is even slower than the rates at which they grow in the absence of a fast growing neighbor. A simple mathematical illustration of this model can be given in terms of the Wagner diffusivity. If the concentrations at two boundaries of a phase layer are C_{iR} and C_{iL} respectively, and the homogeneity region within the phase layer $\Delta C_i = C_{iR} - C_{iL}$ is very narrow, the Wagner diffusivity can be defined as:

$$D_i = \frac{1}{\Delta C_i} \int_{C_{iL}}^{C_{iR}} \tilde{D}(C) dC$$

where C is the atomic fraction of one element, $\tilde{D}(C)$ the interdiffusion coefficient.

In the case of two simultaneously growing phases 1 and 2 with significantly different integrated Wagner diffusivities $D_1\Delta C_1 \gg D_2\Delta C_2$, their thickness ΔX_i obeys the following parabolic laws:

$$\Delta X_1 \approx \sqrt{2D_1\Delta C_1 t}^{1/2}$$

$$\Delta X_2 \approx \frac{2D_2\Delta C_2}{\sqrt{2D_1\Delta C_1}} t^{1/2}$$

so that:

$$\frac{\Delta X_2}{\Delta X_1} \approx \frac{D_2\Delta C_2}{D_1\Delta C_1} \ll 1$$

Thus, according to this model, other phases exist and grow but far too slowly, and their layers are too thin that it is difficult to detect them.

K. N. Tu [38,39] examined the influence of the interfacial reaction barriers on the intermediate phase growth kinetics in binary system, and proposed that some phase would not form due to the suppression effect of the interfacial barriers.

Fig. 2.9 Schematic of concentration profile of A atoms in the A-B diffusion couple [38]

Suppose two phases, $A_\beta B$ of thickness x_β and $A_\gamma B$ of thickness x_γ , are growing simultaneously as shown in Fig. 2.9, the growth of the two phases can be expressed as below taking into account the effective interfacial reaction barriers κ_β^{eff} and κ_γ^{eff} of each phase:

$$\frac{dx_\beta}{dt} = G_\beta j_\beta^A - G_{\beta\gamma} j_\gamma^A$$

$$\frac{dx_\gamma}{dt} = G_\gamma j_\gamma^A - G_{\gamma\beta} j_\beta^A$$

where $j_\beta^A = \frac{\Delta C_\beta^{eq} \kappa_\beta^{eff}}{1 + x_\beta \kappa_\beta^{eff} / \tilde{D}_\beta}$ and $j_\gamma^A = \frac{\Delta C_\gamma^{eq} \kappa_\gamma^{eff}}{1 + x_\gamma \kappa_\gamma^{eff} / \tilde{D}_\gamma}$ are steady state diffusion fluxes of

A atoms in $A_\beta B$ and $A_\gamma B$ phases respectively, ΔC_β^{eq} and ΔC_γ^{eq} are the equilibrium homogeneity regions of the two phases in the absence of interfacial reaction barriers, G_β , G_γ , $G_{\beta\gamma}$ and $G_{\gamma\beta}$ are defined as follows:

$$G_\beta = \Omega_0 (1 + \beta)^2 \left(\frac{1}{\alpha - \beta} + \frac{1}{\beta - \gamma} \right)$$

$$G_\gamma = \Omega_0 (1 + \gamma)^2 \left(\frac{1}{\beta - \gamma} + \frac{1}{\gamma - \delta} \right)$$

$$G_{\beta\gamma} = G_{\gamma\beta} = \Omega_0 \frac{(1 + \beta)(1 + \gamma)}{\beta - \gamma}$$

where Ω_0 is the volume per A or B atom.

The condition for $A_\beta B$ to grow is $dx_\beta / dt > 0$, and thus follows:

$$r = \frac{j_\beta^A}{j_\gamma^A} > \frac{G_{\beta\gamma}}{G_\beta} = \frac{(1 + \gamma)(\alpha - \beta)}{(1 + \beta)(\alpha - \gamma)} = r_1$$

where r is the ratio of the diffusion fluxes j_β^A and j_γ^A . Analogously, the similar

condition for growth of $A_\gamma B$ is:

$$r = \frac{j_\beta^A}{j_\gamma^A} < \frac{G_\gamma}{G_{\gamma\beta}} = \frac{(1+\gamma)(\beta-\delta)}{(1+\beta)(\gamma-\delta)} = r_2$$

Obviously, r_1 and r_2 only depend on the compositions of the compounds and $r_2 > r_1$. The two phases can grow together only if $r_1 < r < r_2$, otherwise one phase would shrink. Therefore, which of the two phases $A_\beta B$ and $A_\gamma B$ will grow or shrink will depend on the value of r determined by the experimental conditions.

During the period when the two compound phases grow interface-controlled concurrently, r can be determined as:

$$r = \frac{\Delta C_\beta^{eq} \kappa_\beta^{eff}}{\Delta C_\gamma^{eq} \kappa_\gamma^{eff}}$$

It is most likely that either $r > r_2$ or $r < r_1$ will be satisfied because $r_1 < r < r_2$ is a rather narrow region, and hence only one phase, e.g. $A_\gamma B$ if $r < r_1$, could grow as the first phase. If the growth kinetics of $A_\gamma B$ changes to diffusion control after some time, r becomes to be determined by:

$$r = \frac{\Delta C_\beta^{eq} \kappa_\beta^{eff}}{\Delta C_\gamma^{eq} \tilde{D}_\gamma} x_\gamma.$$

As x_γ increases, there is a point of time when r becomes $> r_1$, after which $A_\beta B$ would start to grow. This is also a time when x_γ reaches the critical thickness x_γ^{crit} as:

$$x_\gamma^{crit} = r_1 \frac{\Delta C_\gamma^{eq} \tilde{D}_\gamma}{\Delta C_\beta^{eq} \kappa_\beta^{eff}}$$

Once growth of $A_\beta B$ becomes diffusion controlled too, r can be expressed as:

$$r = \frac{\Delta C_\beta^{eq} \tilde{D}_\beta}{\Delta C_\gamma^{eq} \tilde{D}_\gamma} \frac{x_\gamma}{x_\beta}.$$

It can be shown that, whatever the initial ratio of x_γ/x_β , the diffusion system would self-regulate to maintain the coexistence of the two phases until a fixed thickness ratio when both layers grow proportional to $\sqrt{t}$. However, if the material supply is cut off before x_γ reaches x_γ^{crit} , the second phase would not be formed.

Gusak [40,41] also speculated on a suppression effect on the intermediate phase growth from a diffusion point of view. In this model, a phase is supposed to start growing only from nucleus of a certain critical size. This nucleus is created as a result of inevitable heterophase fluctuations in a sharply inhomogeneous system and takes part in diffusive interactions. Evidently, fluxes change abruptly when passing across the boundary of the new nucleus. Some nuclei can shrink to undercritical size if the neighboring phases have larger diffusivity and comparative thickness, which is called the “diffusive suppression by the neighboring fast growing phase”. For example, if the phase 2 with composition C_2 and narrow homogeneity range $\Delta C_2 \ll 1$ nucleates between a growing phase 1 and end material B as shown in Fig. 2.10, the movement of the two interfaces of phase 2 with some velocity u can be determined as follows:

$$(C_2 - C_1)u_{12} = \frac{D_1 \Delta C_1}{\Delta x_1} - \frac{D_2 \Delta C_2}{\Delta x_2}$$

$$(1 - C_2)u_{2B} = \frac{D_2 \Delta C_2}{\Delta x_2} - 0$$

Thus, the growth of phase 2 can be written as:

$$\frac{d\Delta x_2}{dt} = u_{2B} - u_{12} = \frac{1}{C_2 - C_1} \left(-\frac{D_1 \Delta C_1}{\Delta x_1} + \frac{1 - C_1}{1 - C_2} \frac{D_2 \Delta C_2}{\Delta x_2} \right)$$

If phase 2 is a critical nucleus of size l_2^{cr} , it can be noticed that if the thickness of phase 1, Δx_1 , is smaller than a certain critical size Δx_1^*

$$\Delta x_1 < \Delta x_1^* = \frac{1 - C_2}{1 - C_1} \frac{D_1 \Delta C_1}{D_2 \Delta C_2} l_2^{cr},$$

the growth of phase 2 will be suppressed since at this time

$$\frac{d\Delta x_2}{dt} < 0.$$

If the diffusivity of phase 1 is much larger than phase 2, $D_1 \Delta C_1 \gg D_2 \Delta C_2$, the suppression will be more obvious as the “shark phase” 1 will consume the diffusion flux and prevent the nucleation of phase 2 during an incubation period τ given as:

$$\tau = \frac{C_1(1 - C_1)}{2D_1 \Delta C_1} (\Delta x_1^*)^2 = \frac{C_1(1 - C_2)^2}{2(1 - C_1)} \frac{D_1 \Delta C_1}{(D_2 \Delta C_2)^2} (l_2^{cr})^2$$

Fig. 2.10 Schematic of phase 2 nucleation at interface between phase 1 and B [41]

Both the interfacial barrier model and diffusive suppression model predict from different perspectives the suppression/growth criterion associated with a certain critical thickness of the first growing phase, under which growth of other phases is kinetically suppressed. However, the variables and constants involved in these models are practically difficult to measure, making them not easily applicable in the real practice. Moreover, none of the models has considered the nucleation barrier of the new phase. In fact, nucleation is the

initial process during the formation of any new phase, and if there is a nucleation barrier, it has to be superimposed on the interfacial barrier and diffusive suppression effects.

Subsequently, Gusak [42] conducted a comprehensive thermodynamic study on the effects of chemical potential gradients on the nucleation of the new phase as a result of reactive diffusion, and derived the suppression criteria in several specific situations. For nucleation of the phase 2 (concentration C_2) between a growing intermediate phase 1 (concentration C_1) and a dilute solution β as shown in Fig. 2.11, the nucleation of phase 2 will be suppressed if the following condition is satisfied:

$$\frac{\Delta x_1}{l_1^{cr}} < 5 \frac{C_2 - C_1}{C_1(1 - C_1)} \left(\frac{\Delta g_{10}}{\Delta g_{20}} \right)^2 \quad (2.1)$$

where Δx_1 is the critical size of phase 1, Δg_{10} and Δg_{20} are the driving force per mole of atoms for the reactions $A + B \rightarrow 1$ and $1 + \beta \rightarrow 2$ respectively, l_1^{cr} is the standard critical size of nucleus of phase 1. Before the phase 1 layer reaches the critical thickness, Δx_1 , this “vampire” phase suppresses all nucleation attempts of phase 2, so that the latter is present only “virtually” and is not being detected. This approach is more practical as compared to the previous two models since it involves only the free energy change for the reactions which are measurable and available in the literature.

Fig. 2.11 Schematic of phase 2 nucleation between intermediate phase 1 and β [42]

2.2.5.2 Phenomenological Models in Al-Au System

Majni *et al* [18] alternatively constructed a diagram based on experimental observations to demonstrate the evolution path of Al-Au thin film interactions by integrating a time axis to the equilibrium phase diagram as copied in Fig. 2.12. The diagram shows, in order to form one desired compound, two other phases are needed. The arrows in the diagram start from these two phases and end at the growing compound. For example, in order to have AlAu compound (denoted as 3), Al₂Au (2) and AlAu₂ (4) are required. Al₂Au is formed by reaction between Al (1) and AlAu₂ (4), and AlAu₂ grows at the expense of Al (1) and Al₂Au₅ (5). Al₂Au₅ is then the first phase that should be formed between elemental Al (1) and Au (7). The reverse of this deduction would be the sequence of intermetallic formation.

Fig. 2.12 Diagram showing how a time axis can be added to the phase diagram [18]

R. Pretorius and coworkers [43,44] developed a theory based on the effective heat of formation (EHF) of each Al-Au intermetallic in an attempt to explain the formation of Al_2Au_5 as the first intermetallic in thin film diffusion couples. The theory proposed the term of “limiting element” which refers to the element short of supply at the interface as compared to that needed to form a particular intermetallic. Therefore, the EHF of this intermetallic phase, $\Delta H'$, could be defined as:

$$\Delta H' = \Delta H^o \times \left(\frac{\text{effective conc. of lim. element}}{\text{compound conc. of lim. element}} \right)$$

where ΔH^o is the heat of formation of an intermetallic in equilibrium, and could be calculated as a function of concentration. The diagram of $\Delta H'$ could be constructed by plotting the heat of formation, ΔH^o , of a specific compound at its compositional concentration and completing the triangle whose base connects the two end points of the concentration axis. Fig. 2.13 shows the Al-Au phase diagram with the addition of the

EHF diagrams for the five Al-Au intermetallics. Since the activation energy of solid state diffusion is proportional to the melting point of the solid, the greatest mobility and the most effective intermixing of atoms at a reaction interface are most likely to take place at the composition of the lowest eutectic (or liquidus) on the phase diagram, which could be chosen as the effective concentration of the interacting elements when they are initially brought into contact. It can be seen from Fig. 2.13 that the lowest eutectic in the phase diagram exists at 525°C with 78 at.% of Au and 22 at.% of Al. The EHF of Al_2Au_5 at this concentration (the intersect with the dashed line) is so close to that of AlAu_2 that they both could appear as the first phase depending on the experimental conditions.

Fig. 2.13 Effective heat of formation diagram and phase diagram for Al-Au system [43]

2.3 Al-Au Intermetallic Growth in Wire Bonds

The system of Al-Au came into public sight largely because of its application in wire bond technology. The interdiffusion of two metals in wire bond is quite different to the case in thin film couples, not only because of the substantial difference of quantities involved and the geometry of the components, but also because of the bonding process which introduces heat, pressure and severe deformation. To understand the difference, it is necessary to briefly introduce the wire bonding technology before delving into the intermetallic growth in wire bonds.

2.3.1 A Brief Introduction of Wire Bonding Technology

Wire bonding technology remains a leading interconnecting technology in the microelectronic industry, especially in the chip level packaging. The microelectronics market consumes 14 billion feet of bonding wire, and more than 1 trillion wire bonds are made in the world every year, in which gold bonding wire is presently a US\$1billion business with a growth rate of >10% per annum [45]. However, challenges from the new technologies such as flip chip in high I/O count, fine pitch packaging applications seem to weaken its prevalence [46]. On the other hand, the relentless pressure in microelectronic industry to reduce costs, device sizes, as well as to increase performance and reliability has been a major driving force for the development of new bonding materials and processes [47–50]. Therefore, considerable research effort has been expended and innovations made to sufficiently develop the potential of wire bonding to survive the competition.

There are two different types of wire bonds, namely ball bonds and wedge bonds. In ball

bonding, a small capillary is used through which a fine gold wire passes. A small portion of the wire protrudes out of the capillary and its end melts under the application of an electronic-flame-off system to form a ball that is usually referred to as free air ball (FAB). The capillary lowers and squashes the ball onto the bonding pads on the silicon die. The combination of heat, pressure, ultrasonic energy as well as time will cause the ball to plastically deform and interdiffuse with the pad metallizations underneath at the atomic level, hence forming the first wire bond. The capillary then rises and moves along a predetermined trajectory to the second pad site on the substrate, during which a well-shaped wire loop is developed. The second bond is formed the same way as the first one except that it is shaped like a wedge or stitch. The bonding process repeats after the wire breaks slightly above the wedge [51]. Fig. 2.14 schematically represents the ball bonding process flow.

Fig. 2.14 Schematic illustration of ball bonding process [51]

Wedge bonding is very popular for bonding aluminum wire. In this technique, a bonding wedge with a through hole from the backside to the bottom side is utilized. The wire is fed through this hole at an angle of 30-60°. The wedge descends onto the first bond location on the IC chip to stave the wire by applied force and ultrasonic vibration, leaving a wedge-shaped bond on this site. Next, the wedge rises and, following a precisely defined looping motion, moves to the second pad site where the second bond is created as a result of force and vibration. The bonding process recycles as soon as the wire breaks under tear force. A typical process flow of wedge bonding is shown in Fig. 2.15.

Fig. 2.15 Schematic illustration of wedge bonding process [51]

The major difference between the above two bonding processes is that FAB is required at

the beginning of each bonding cycle in ball bonding at an elevated temperature of about 150°C, whereas in wedge bonding the wire is directly bonded to the pad at room temperature. Ball bonding is superior over wedge bonding in terms of production efficiency.

Gold, aluminum [52–54] and copper [55–57] are the most popularly used bonding wire materials, each of which possesses its own advantages and disadvantages. Gold is still the predominant material used in ball bonding due to its easy deformation capability and its resistance to oxide formation. However, pure gold wire, manufactured through a series of elaborately performed drawing and annealing steps [45][58,59], is very soft. Therefore, various dopant elements such as silver (Ag), calcium (Ca), platinum (Pt), aluminum (Al), and palladium (Pd) have been added to gold in some specific applications [60,61] to increase the wire strength particularly when wire diameter is extremely small.

Wire bonding creates various metallurgical coupling systems depending on the wire and pad materials, giving rise to specific benefits as well as reliability issues such as intermetallic growth [62], element diffusion and migration [63], interfacial corrosion and degradation, crack dynamics etc. The typical metallurgical bonding systems tested for wire bonding process are listed in Table 2.2.

Table 2.2 Typical intermetallic compounds (IMC) in some bonding systems [64]

Metallurgical System	IMC	Reliability Issues
Au-Au	—	Very reliable, no interface corrosion and degradation, highly sensitive to surface contamination.
Au-Al	Au ₅ Al ₂ , Au ₄ Al, Au ₂ Al, AuAl,	IMC forms easily even at room temperature, reliability is always a key

	AuAl ₂	concern.
Au-Cu	Cu ₃ Au, AuCu, Au ₃ Cu	IMCs are ductile, but can still degrade bond strength at higher temperature. Impurity levels in copper and cleanliness of the bonding surface are crucial factors for reliability.
Au-Ag	—	No IMC forms at the interface. Very reliable for long-term usage. The only concern is to eliminate sulfur in the system.
Al-Al	—	No IMC forms, extremely reliable.
Al-Ag	Very Complex	Kirkendall voids occur in this system, In the presence of moisture, the bonds degrade rapidly. Process for making Al-Ag bonds is very tough.

Bonding mechanism is one of the most divergent issues in understanding wire bonding technology. As of today, even issues like the role of heat during bonding process still arouses much controversy. A qualitative description treats the ultrasonic wire bond formation as a type of deformation weld [64,65]. The metal wire is softened by ultrasonic energy and the clamping force scrubs and deforms the softened wire against the bonding pad, crushing the oxides and contaminants on the pad surface aside or to the low lying asperities, thus making a clean contacting surface. A few milliseconds later, metallurgical bonding appears to initiate from the periphery of the bonds and spreads towards the center. Ultrasonic energy is absorbed into the entire bonding area including wire, interface and bond pad. Little deformation occurs in the center of the bonds, so oxides and contaminants could remain in this area, leaving this part sometimes unbonded.

2.3.2 Interface Interactions in Al-Au Wire Bond

The formation of intermetallics in wire bonds was initially found to be represented by the resistance change of the connection upon heating. The root cause accounting for this phenomenon was ascribed to the fact that intermetallics, such as Al_2Au_5 and AlAu_4 , possess higher resistivity as compared to gold and aluminum metals. When Kirkendall voids aggregate to develop a separation gap between intermetallic phases, the resistance change could be even more distinct [66–68]. A typical resistance vs. time diagram upon annealing obtained by L. Maiocco *et al* [69] is reproduced in Fig. 2.16. When wire bonds, made by bonding a $33\mu\text{m}$ diameter gold wire to $1.2\mu\text{m}$ thick Al metallization, were heat treated in $77\text{--}277^\circ\text{C}$ temperature range, the resistance increase, ΔR , was linearly dependent upon the square root of time, $t^{1/2}$. This relationship could be more precisely described by an expression: $\Delta R = c \times t^n$, where c is a constant and n the optimized time exponent found to be around 0.4 ± 0.02 for all temperatures. Concomitant with resistance change, a peripheral ring of intermetallic was observed around the bond base with the depletion of Al taking place around the ring. All five Al-Au intermetallics were identified in the bonds and found to go through transformation during heating. AlAu_2 was reported to dominate in wire bonds for short annealing times and it transforms to Al_2Au_5 and AlAu_4 for extended times. Voids initially appear in a single phase, e.g. AlAu_4 , or at interfaces, e.g. $\text{Al}_2\text{Au}_5/\text{Au}$ interface, and coalesce into a line to completely separate the bond and base metal. Intermetallic growth and void coalescence resulting in ball bond failures in shear tests can be classified into 6 categories as shown in Table 2.3 [70].

Fig. 2.16 Resistance change in wire bonds during annealing [69]

Much notable work on Al-Au intermetallics formation in wire bonding has been published, under the conditions of different bonding parameters, materials and environments. A general consensus has been reached that when gold bonding wire is brought into intimate contact with the aluminum pad metal on Si chips under the application of pressure and ultrasonic vibration, a thin layer of intermetallic is formed at the bond-pad interface. The pad metal usually contains trace amounts of alloy elements such as Cu (typically 0.5 wt.%) and/or Si (typically 1 wt.%), but the intermetallics are formed basically between Au and Al with the minor additions being accommodated within or around the intermetallic phases.

Table 2.3 Wire bond shear failure modes [70]

Bond failure mode	Failure description
1	Shear failure initiates in Al film. Often the initial plastic flow of Al is followed by subsequent shear and fracture in the Au. Typical of as-bonded and low temperature/low time samples with Cu and Si additions to metallization.
2	Shear failure initiates in Au ball, subsequent failure in Al. Frequently Al and Au surfaces alternate. Common in as-bonded and low temperature/low time samples of pure Al and Al-Cu-Si metallizations.
3	Original bond area remains intact. Entire failure is in the Au. Variation of this type includes Au surrounded by intermetallic ring or Au pad with small holes or cracks. This is the most common failure mode.
4	Ductile Au failure with some intermetallic removed, showing underlying films. Occur at long times at high temperature. Size of holes varies from 5% of bond area to 90%.
5	Ductile Au failure with some intermetallic and underlayer removal, revealing SiO ₂ film. Occur at longest times at high temperature.
6	Entire Au ball and central intermetallic are removed. SiO ₂ film surrounded by intermetallic ring remains at bond pad. Type 4 and 5 will finally progress into this type.

A recent study by C. D. Breach and F. Wulff portrays the evolution of intermetallic growth in gold ball bond upon annealing [71,72]. In their study, 25 μ m diameter gold wire was bonded to 1 μ m thick Al pad and annealed at 175°C up to 1000 hours. The evolution of intermetallics in early hours of annealing (<10h) is reproduced in Fig. 2.17. The as-bonded wire bond showed discrete islands of intermetallics across the ball diameter, while intermetallics grew both vertically into the gold ball and laterally within the ball contacting area during subsequent heat treatment.

Fig. 2.17 Early growth of intermetallics in gold ball bonds [71]

As shown in Fig. 2.18, extended annealing did not cause the thickness of intermetallics to change significantly, but enabled the growth to expand into the surrounding Al film at 50h concomitant with the formation of voids. Although the intermetallics under the ball center seemed to have had no further change, the region near the ball edge experienced an accelerated growth such that a ‘hump’ was developed as indicated by the arrows at 200h.

Fig. 2.18 Intermetallics growth during extended heat treatment [71]

The intermetallic phases in wire bonds were identified in sequence to be columnar Al_2Au_5 after 2h annealing, and subsequently, coexistence of Al_2Au_5 at the ball center with two layers of AlAu_4 after 200h annealing as shown in Fig. 2.19 (a). The formation of a second layer of AlAu_4 was attributed to reducing the stresses between adjacent phases due to different unit cell and molar volumes. At the periphery of the ball, AlAu_2 was formed as shown in Fig. 2.19 (b) probably because of the reduced supply of Au forcing the transformation of Al_2Au_5 to AlAu_2 .

Fig. 2.19 SEM micrographs showing (a) coexistence of Al_2Au_5 with two layers of AlAu_4 and (b) intermetallic phases in a wire bond annealed at 175°C for 200 hours [71]

2.4 A Review of Oxidation

The presence of aluminum in alloys always leads to improvement of oxidation resistance of the materials [73,74], except when the resulting alumina scale is not continuous and therefore less protective [75,76]. Al is frequently intentionally added to many alloys [77,78] to improve oxidation resistance.

Fig. 2.20 Schematic illustration of a wire bond showing the location of oxidation

In wire bonding process, however, the oxidation of Al is regarded detrimental to the quality of the wire bonds. It has been proven that the aluminum bond pad oxidation is damaging to the formation of good contact between the gold wire and aluminum metallization, resulting in a poor strength bond. Recently, a new wire bond failure mechanism has been proposed involving the oxidation of aluminum-gold intermetallics at the bonding interface [72]. This proposal argues that the intermetallics could oxidize from the periphery of the bond (see Fig. 2.20) in the presence of humidity and air. The chemical reaction and phase transition within the oxide scales might lead to the formation of voids or cracks, which could propagate along the bond interface causing failure.

Literature on oxidation of Al-Au intermetallics is quite scarce. In the next section, we review the general characteristics and principles of oxidation applicable to Al alloys.

2.4.1 Basic Principles of Oxidation

Generally, oxidation of metals or alloys involves three consecutive steps as follows [79–82]:

- 1) Dissociation of impinging gas phase molecules on the metal surface;
- 2) Growth of the chemisorbed species island in the metal matrix;
- 3) Oxide nucleation around the chemisorbed islands with appropriate size.

For instance, a model for oxide layer growth on a clean Al surface in moisture has been set up. This model assumes that water molecules are adsorbed dissociatively on Al surface, resulting in the presence of oxygen atoms and hydrogen as well. The adsorbed oxygen atoms act as oxide nuclei and grow laterally via island formation [83]. This mechanism was confirmed by G. J. van der Kolk and M. J. Verkerk [84].

Various studies have been done on the oxidation kinetics of Al alloys by means of thermogravimetry. Almost all of these studies report a parabolic growth behavior [85–89]. Fig. 2.21 shows typical weight gain vs. exposure time curves under different temperatures in kinetics study for Ti_3AlC_2 . This parabolic behavior can be expressed by Equation (2.2):

$$(\Delta W / A)^2 = k_p t \quad (2.2)$$

where $\Delta W / A$ is the mass uptake per unit surface area, k_p is the parabolic rate constant and t is time.

From each curve at a certain temperature, the value of k_p can be calculated. On the other hand, k_p is related to temperature by Equation (2.3):

$$k_p = k_0 \times \exp\left(-\frac{Q}{RT}\right) \quad (2.3)$$

where k_0 is the pre-exponential factor, R the gas constant, T the absolute temperature, and Q the activation energy of oxidation. Equation (2.3) can be rewritten as follows:

$$\ln k_p = -\frac{Q}{RT} + \ln k_0 \quad (2.4)$$

From a plot of $\ln k_p$ and $1/T$, the value of Q can be obtained.

Fig. 2.21 Parabolic oxidation kinetics for Ti_3AlC_2 [87]

In contrast to parabolic growth, linear oxidation growth is also sometimes observed especially in the initial oxidation stage, indicating the rapid establishment of the oxide scale. As oxidation proceeds, the separate oxide islands on the surface merge together and a continuous scale gradually comes into being. The linear kinetics slow down and become parabolic type subsequently.

2.4.2 Oxidation Characteristics of Al-Au Intermetallics

Although there have been enormous research activities on oxidation of various aluminum alloys, not much effort has been input to characterize oxidation of Al-Au intermetallics. Actually, gold wire bonded to aluminum bond pad arouses attention about the oxidation of Al-Au intermetallics at the bond periphery where they are exposed to the ambient until encapsulation. This could act as a new wire bond failure mechanism in humid, high temperature environment. On the other hand, this system is relatively oxidation resistant due to the inert nature of Au and the oxidation passivation of Al. The oxide scale is extremely thin (e.g. 10 nm) so that conventional techniques to investigate the surface chemical compositions may not be usable.

H. Piao *et al* [80][90–93] has extensively explored the oxidation behavior of Al-Au thin films under varying conditions using X-ray photoelectron spectroscopy (XPS). In their studies, gold thin films were ion sputter deposited to certain thickness on the polished and ion beam cleaned aluminum bulk material surface. Two major Al-Au intermetallics, AlAu_2 and Al_2Au , were formed in ultra high vacuum by precisely controlling the alloying temperature and dwelling time, e.g. 200°C, 2h for AlAu_2 or 300°C, 3h for Al_2Au . The oxidation procedures include short time in air, long time in air and exposure to moist air with doses ranging from 0.1 to 1×10^9 Langmuir.

In the short time air exposure study, i.e. 24 h in air at room temperature, shifting of the binding energy (b.e.) peaks on the XPS spectra were found for both AlAu_2 and Al_2Au . The peak transition for Al_2Au alloy is illustrated in Fig. 2.22. Each dotted line in the figure is a fitting component corresponding to a particular compound and the continuous curves are fitted to the experimental XPS data using these components. Thus, the

obtained XPS spectrum can be deconvoluted into several different but reasonable components when a good fitting is achieved. Before exposure, the peak corresponding to Al_2Au stands at 85.90 ± 0.05 eV in Fig. 2.22(a), which is prominently shouldered by a sub-peak at 85.05 eV representing AlAu_2 in Fig. 2.22(b). A minor peak in Fig. 2.22(b) at 84.0 eV can be deconvoluted and identified as Au metal. It is then believed that the original Al-rich Al_2Au matrix undergoes significant phase transition to AlAu_2 , the Au-rich phase, due to the depletion of Al at the near surface region. Al has been consumed to form oxide such that even metallic gold is present at some locations.

Fig. 2.23 demonstrates the peak shifting for AlAu_2 . In this case, the peak for AlAu_2 at 85.01 eV diminishes after exposure in combination with the occurrence of two additional peaks at 84.90 eV and 84.45 eV respectively. Since AlAu_2 is an Au-enriched phase, the appearance of these two peaks could be attributed to the formation of phases with even higher Au content.

For both Al_2Au and AlAu_2 , the outward diffusion of Al from the interior seems insufficient to offset the loss in the outer area. Thus, transformation to phases of even higher Au content is likely to take place. Another interesting finding in this study is that the oxidized alloy would recover to the initial state after a reheating treatment. An example is given for AlAu_2 in Fig. 2.23(c). The additional shoulders on the oxidized spectrum disappear completely after a second heat at 120°C , seemingly suggesting the reversibility of oxidation. This surprising recovery of oxidized Al-Au intermetallics appeared several times in H. Piao's publications. However, the underlying mechanism accounting for this phenomenon remains unknown. In addition, no evidence has shown the oxidation of Au in the materials.

(a) Before air exposure

(b) After air exposure

Fig. 2.22 Au 4f binding energy spectra for Al_2Au before and after 24h air exposure [91]

During prolonged exposure times, viz. 3 months in ambient at room temperature, the transition to Au-enriched phases is only observed within the beginning 10 days for each intermetallic. After 10 days, it seems that no significant change occurs according to the

peak intensity on the spectrum, evidencing the establishment of a continuous oxide scale.

Fig. 2.24 gives the detail of XPS spectra.

Fig. 2.23 Au 4f binding energy spectra for AlAu_2 : (a) before 24h air exposure; (b) after 24h air exposure; (c) after reheating at 120°C for 1h [91]

Fig. 2.24 Au 4f binding energy spectra for (a) Al_2Au and (b) AlAu_2 after different exposure durations [90]

In the moist oxidation study, the sample was made without intentional control of the composition so that Al_2Au and AlAu_2 were both present in the alloy. It was placed in a

humidity-filled chamber attached to the XPS spectrometer to oxidize with doses ranging from 0.1 to 1×10^{14} Langmuir. Fig. 2.25 represents the evolution of the XPS spectra. As previously discussed, the Al_2Au peak diminishes while AlAu_2 peak prevails as humidity dose increases.

Fig. 2.25 Au 4f binding energy spectra for Al-Au alloy in moist oxidation conditions [80]

When compared to Al metal under the same oxidation conditions in terms of oxide thickness, there is a remarkable similarity between these two at all exposure dose levels (Fig. 2.26). This can be construed as Al is the only contributor to oxidation in the alloy. It is also found that along with the oxide thickness increase upon increasing humidity dose, the ratio of peak intensities of AlAu_2 and Al_2Au , i.e. $I_{\text{AlAu}_2} / I_{\text{Al}_2\text{Au}}$, increases almost proportionally (Fig. 2.27). Transformation from Al_2Au to AlAu_2 involves release of Al atoms, whereas thickening of scale requires consumption of Al atoms. Therefore, it is

believed that Al atoms diffusing into the oxide scale are probably from the location where phase transformation takes place.

Fig. 2.26 Oxide thickness of Al-Au alloy and Al metal during moist oxidation [80]

Fig. 2.27 Relationship between oxide thickness and the I_{AlAu_2} / I_{Al_2Au} ratio [80]

During the initial stage of oxidation, the Oxygen / Aluminum ratio was found to be less than the stoichiometric value of alumina (1.5), suggesting that the scale at this stage is discontinuous and rather defective. A nearly stoichiometric value was obtained at higher humidity dose (Fig. 2.28). However, when the dose is extremely high, the ratio rises to 2, larger than stoichiometric value. This is thought to be the hydration of the oxide formed. In this case, oxygen appears in three forms: Al_2O_3 , Al-OOH and $\text{Al-H}_2\text{O}$.

Fig. 2.28 Evolution of Oxygen / Aluminum concentration ratio with exposure dose [80]

2.5 Formulation of Scope and Objectives

Al-Au system plays a fundamental and important role in wire bonding industry. As the microelectronic industry relentlessly pursues increasing integration of ultra large scale IC and miniaturization of a single chip, the bonding wire diameter is to be steadily reduced from the conventional $25\mu\text{m}$. It has already reached $18\mu\text{m}$ at present. This makes the quality and reliability of the shrinking wire bonds more crucial than ever. Enhancement of

the reliability of Al-Au wire bond requires a comprehensive knowledge covering intermetallic formation and transformation, and their growth and degradation.

Based on the above review of available literature, it is clear that Al-Au intermetallics have been observed and investigated either in thin films or in wire bonds, but the exact types of phases formed and their transformation sequence differ significantly among the published works. Various studies have been carried out under a wide range of conditions, but the effects of the two critical parameters, temperature and time, have not been properly identified to generate a phase transformation diagram suitable for understanding the consequences in isothermal annealing around temperatures used in industrial packaging.

On the issue of diffusion mechanism, which is inherently related to the growth of intermetallics, some researchers assumed that Au is the main diffusant on the premise that diffusion should occur faster in the lower melting point component, to explain some specific phenomenon in their experiments or to formulate a curve fitting model. However, none of the previous studies could provide direct experimental evidence, to prove or disprove, that Au is the predominant diffusant in this system.

Identification of intermetallics have been performed predominantly by XRD which has a lower limit of detectability when some phases are in small quantities. Further, the microstructure and morphology of the intermetallics at the interface have not been characterized. Therefore, attempts will be made in this project to utilize TEM techniques also to characterize the microstructure of the interface, in addition to the conventional method of XRD.

Two selected Al-Au intermetallics, namely Al_2Au and AlAu_2 , have been proven to oxidize at room temperature, leading to phase transformations. Thus, wire bond degradation due to intermetallic oxidation might become a serious practical problem. More importantly, accelerated oxidation could occur when intermetallics are subjected to high temperatures in the range 175-200°C during manufacture. This has not been examined to any significant depth. Moreover, the predominant intermetallic detected in Al-Au wire bonds in the long term is the Au-richest AlAu_4 but its oxidation behavior does not appear to have been studied. Even basic information such as XPS binding energy peak positions of Au and Al in AlAu_4 is not reported in the literature. Hence, there is a need to study the oxidation behaviors of the common Al-Au intermetallics in some detail.

This project is proposed to address the issues that are seemingly neglected with respect to the Al-Au binary system, and to clarify experimentally the phase formation in situations where conflicting reports have been published. With this view, the following objectives and tasks are formulated:

1. Identify the intermetallics in Al-Au thin films with distinct Au:Al ratios upon isothermal annealing at different temperatures to propose an intermetallic transformation diagram.
2. Provide unambiguous identification of the intermetallics and characterize their microstructures.
3. Clarify the diffusion phenomena and attempt to simulate the intermetallic growth.
4. Characterize the oxidation kinetics of the common intermetallics.

Since this is an investigation of fundamental phenomena, convenient samples will have to be designed and produced, which will facilitate easy characterizations. Actual wire bonds

are somewhat difficult to characterize because of their small size. Therefore, we shall use thin films and bulk samples, almost exclusively, in this study.

Chapter 3 Experimental Procedures

This chapter is dedicated to detail description of the material fabrication and identification techniques, sample preparation procedures and equipment operation parameters.

3.1 Material Preparation Procedures

3.1.1 Thin Film Deposition and Annealing

For interface interaction investigation of Al-Au system, thin film diffusion couples were used. The thin film samples were deposited using MSS3 Diode-magnetron RF/DC sputtering system on the commercially thermal treated 6 inch wafers. The SiO₂ layer on the substrate is used to prevent interaction between Si and the metals deposited. The specifications of the substrate wafer are tabulated in Table 3.1.

Table 3.1 Specifications of the substrate Si wafer

Items	Specifications
Size	6 inch
Orientation	(1 0 0)
Type	N type
Wafer thickness	650 - 700 μ m
Surface finishing	Single side polished
Resistivity	1-20 ohm·cm
Flatness	1 primary flat
Thermal treatment	4000Å $\pm$ 5% thermal oxide on both sides

Gold and aluminum targets both of 99.99% purity were used for deposition. The thickness of gold was fixed as $1\mu\text{m}$, while two sets of aluminum layer thicknesses, $0.3\mu\text{m}$ and $1\mu\text{m}$, were chosen. This was designed to simulate the two situations where gold and aluminum are of equivalent quantities in one case and gold is in excess in the other. For each thin film structure, aluminum was deposited first onto the wafer followed by gold without breaking the vacuum in deposition chamber so that the capping gold layer would be protective. The sample stage was rotated and maintained at room temperature throughout deposition cycles in order to eliminate the reaction of the two layers. The time for depositing desired film thickness was determined using an experimental graph of sputtering deposition rate as shown in Fig. 3.1. Major conditions for film deposition are tabulated in Table 3.2.

Fig. 3.1 Experimental graph to determine Au and Al thin film sputtering deposition rate

Table 3.2 Major sputtering deposition conditions

	1 μ m Al + 1 μ m Au	0.3 μ m Al + 1 μ m Au
Base pressure (torr) before gas inflow	10^{-6}	10^{-6}
DC/RF power connection	DC	DC
Flow rate of Argon (sccm)	20	20
Working pressure (mTorr)	20	20
Pre-sputtering conditions	Power: 100w Time: 10min for each metal	Power: 100w Time: 10min for each metal
Time of sputtering	Al: 75min Au: 25min	Al: 22min Au: 25min
Deposition power	200w	200w

For each thickness configuration, annealing was done at 125°C, 150°C and 175°C in air in a box oven with temperature control accuracy of $\pm 2^\circ\text{C}$. To minimize the effects of fluctuation in deposition, samples annealed at three temperatures were all sliced from the same wafer substrate and deposited in one deposition cycle. Samples were annealed for durations of 1/4, 1/2, 1, 2, 4, 8, 16, 24 hours and cooled in air. Three pieces of samples were made at every combination of temperature and time.

3.1.2 Solid Intermetallics Production

The solid samples were made for investigations of the oxidation kinetics of Al-Au intermetallics in controlled experiments. Three intermetallic compositions were selected in this project: Al_2Au , AlAu_2 and AlAu_4 , and all the solid Al-Au intermetallics were produced by arc melting. Pure gold and aluminum granules both of 99.99% purity were placed in the Cu container in the stoichiometric ratio of the selected intermetallics. An

argon filled environment in the chamber was made by repeating pumping and filling of argon for several times. Arc was ignited by scrubbing swiftly the torch tip against the electrode stub and maintained for a few seconds to melt and react the two metals. In order to ensure that the composition was homogeneous in the bulk, it was flipped over and remelted several times.

3.1.3 Oxidation of Solid Intermetallics

Nine specimens of 4×2 mm size were cut from the bulks of each composition. They were polished using diamond paste to 1 μm surface finishes and ultrasonically cleaned before putting into the air oven. Heat treatment was conducted at 175°C for durations of 1/4, 1/2, 1, 2, 4, 8, 16 and 24 hours. Care was taken to avoid contaminating the clean surface with any direct human contact. Surface analysis was subsequently conducted to examine the chemical states of elements on the surface after oxidation and to estimate the thickness of oxide layer. Pure Al (99.99%) samples were heat treated and analyzed the same way to provide reference in surface analysis.

3.2 Characterization Techniques

3.2.1 X-ray Diffraction (XRD) for Thin Film Investigation

XRD was used for identifications of thin film Al-Au intermetallics. A Rigaku X-ray diffractometer, equipped with graphite Cu K_α monochromator was used. The diffractometer was operated at 50 kV and 50 mA with Cu K_α radiation ($\lambda=1.54056 \text{ \AA}$) in the 2 θ continuous scanning mode. The sample stage was constantly rotated during the measurement and was set to 10 degree initial tilt angle for deeper X-ray penetration into

the film structure. In order to obtain precise measurements of peak positions, a slow scan rate of 1 degree/min was employed in the range of 20-100 degree. Diffractograms were compared with the Inorganic Crystal Structure Database (ICSD) files of Al-Au intermetallics to determine the exact phases formed.

3.2.2 X-ray Diffraction for Solid Intermetallics

The solid Al-Au intermetallic specimens were verified using a Shimadzu X-ray diffractometer with Cu K α radiation. In order to ensure the homogeneity of the samples, one piece of each composition was manually ground into powder in a mortar. The diffractometer was operated at 50 kV and 20 mA in the 2 θ / θ continuous scanning mode. The scan speed was set to be 1 degree/min in the range of 20-100 degree. Diffractograms were also compared with the ICSD files of the intermetallics concerned to confirm the exact phase.

3.2.3 Field Emission Scanning Electron Microscopy (FESEM)

A Japan Electron Optics Limited (JEOL) 6340F FESEM was used for thickness measurements of the intermetallics formed after annealing at every temperature and time. A slice of 5×3 mm size was split from the annealed sample along a line scribed on the reverse of the substrate, and adhered to the side wall of the observation holder, leaving the cross section of the thin film normal to the electron beam. Three images were taken for each sample at three different locations, from which an average thickness for the overall intermetallic growth in this sample was estimated. An image analyzer software ImageTool (version 3.00) was utilized to measure the area of the entire intermetallic layer after scaling with respect to the scale bar in the micrograph, and a nominal thickness was

obtained by dividing the area by the width of the image.

3.2.4 Transmission Electron Microscopy (TEM)

TEM was utilized in order to examine the microstructure and morphology of the intermetallic phases in the cross section thin film samples, and to provide crystallographic evidence for their identifications.

The cross section thin film TEM samples were prepared as follows. Two pieces of specimens that had undergone the same heat treatment were adhered film to film to form a sandwich structure using the G1 epoxy - a mixture of 10 parts of resin and 1 part of hardening agent. Two dummy wafer discs were glued to the sandwich as the supporting elements. The 4-tier stack was cured at room temperature in the presence of applied clamping force overnight. Heating was avoided during sample preparation to eliminate effects to the intermetallics in the sample. Small slices of the cured stack were cut using the slow speed, precision cutter. One cross section of the slice was mechanically ground flat and then fixed onto an epoxy dabbed 3 mm diameter copper gird with a 1.5 mm diameter hole in the center. The interface line of the two adhered films must be placed in the center of the hole, and must be clear of epoxy which might blur the image under TEM if smeared over the interface line. The sample was cured in air at room temperature for one night. Further thinning of the other side of the slice was performed mechanically down to 20 to 30 μ m thickness. Care was exercised to avoid breaking and cracking of the slice when it was extremely thin.

Perforation was made with ion milling. Large angle ion milling with 8° ion beam alignment on both top and bottom planes of the sample was first conducted to thin the

center area, followed by small angle (3° ion beam alignment) ion bombardment after an eye-shaped crater appeared. Ion milling was stopped when a well sized hole appeared in the center to provide sufficient electron transparent area. Liquid nitrogen was poured into the built-in tank inside the ion miller to reduce heating during ion bombardment.

A JEOL 2000 TEM was used for observations. Selected area diffraction (SAD) patterns were obtained at a camera length L of 30 cm. There is indexed SAD pattern taken at the same camera length for standard Au sample, which is related to the experimental pattern by the expression as below:

$$R_{\text{experiment}} d_{\text{experiment}} = R_{\text{Au}} d_{\text{Au}}$$

where R is the measured lengths of the vectors in patterns, d the interplanar spacing of the crystallographic planes. Therefore, knowing d_{Au} , R_{Au} and $R_{\text{experiment}}$ will allow for calculation of the interplanar spacing of the planes indicated by the selected vectors in the experimental pattern. Screening the suspected intermetallics and comparing the ICSD data list for them with the calculated interplanar spacing values would permit a final indexing of the pattern.

3.2.5 Secondary Ion Mass Spectrometry (SIMS)

SIMS is a very effective surface analysis technique to investigate the element distribution in stacked structures. In this project, SIMS was performed to track the interface movement in the annealed thin film samples to determine the main diffusant in Al-Au system.

The Time-Of-Flight SIMS instrument (TOF-SIMS IV) used herein was manufactured by CAMECA/IONTOF, Germany. It is equipped with three ion guns for analytical and

sputtering purposes, and a reflectron type TOF analyzer. The main analytical gun is a gallium liquid metal ion gun and the other two guns, an argon ion gun and a cesium gun, are used for sputter etching. In the TOF-SIMS instrument, the secondary ion masses are measured by a time-of-flight measurement using the pulsed primary ion beams. The secondary ions generated by each primary ion pulse are accelerated to a constant kinetic energy, and then fly through a field free space before they hit a detector, where their intensity is measured as a function of flight time. Since ions with different masses have different velocities at a given kinetic energy, the measured flight times of the ions can easily be converted to their masses.

Depth profiling was done in negative ion polarity mode in order to develop overall element distribution information. The sputtering area produced by 3 keV Ar ion bombardment was set as $150 \times 150 \mu\text{m}^2$, while the analytical area used for 25 keV Ga impingement as $100 \times 100 \mu\text{m}^2$.

The depth of each sputtered crater was subsequently measured using Tencor Alpha-step[®] 500 surface profiler after SIMS analysis at a consistent stylus force of 12.0 mg and a scan speed of $20 \mu\text{m/s}$. This was used to determine an average sputtering rate from which the depth was estimated for any sputter time. A typical crater depth profile is illustrated as Fig. 3.2.

Fig. 3.2 A typical crater depth profile

3.2.6 Differential Scanning Calorimetry (DSC)

Thermal analysis to detect the melting point of the solid intermetallics could further confirm their compositions, thus DSC measurement was carried out. A NETZSCH 404C instrument was employed after calibrating the equipment using standard samples as suggested in the maintenance manual.

Small pieces of about 20 milligrams were cut from the intermetallic. A flat surface was ground for each specimen to make a good contact with the base of the alumina crucible. Each sample was heated up to 200°C higher than the maximum transformation temperature indicated in the Al-Au phase diagram to ensure the transformation could proceed completely. The baseline measurement was conducted beforehand using the same crucibles and under the same testing conditions. Baseline was subtracted from the detected DSC graphs. Key parameters in DSC tests are listed in Table 3.3.

Table 3.3 Key parameters in DSC measurements

	Heating rate (°C/min)	Holding Time (min)	Maximum Temp. (°C)
Al ₂ Au	10	60	1300
AlAu ₂	10	60	850
AlAu ₄	10	60	800

3.2.7 Thermogravimetry Analysis (TGA)

TGA was involved for oxidation kinetics study of the solid intermetallics. Three specimens of 2×2 mm size were prepared for each intermetallic. All the surfaces were first ground with SiC papers up to 1000 grit size and then were polished using diamond paste down to 1 μm final finishes. After polishing, all the samples were ultrasonically cleaned with acetone for several times to remove the polishing debris and lubricant oil, and then dried for 48 hours in desiccator before subsequent measurements. The mass change of solid intermetallics were measured with a Mettler Toledo TGA/SDTA851° thermogravimetry analyzer. This equipment uses a cantilever balance, on which the sample crucible sits, to precisely detect the trace increase of the sample weight during oxidation. Weight values were shown up to three decimal places in milligram. All samples were heated and oxidized in the purified oxygen atmosphere for 20 hours at 200, 300 and 400°C respectively. The temperatures were meticulously maintained constant with variation within ±0.25°C. The airflow was controlled by a gas controller and set at 50ml per minute all through the tests. The real time airflow was displayed on the LCD panel for monitoring. Prior to testing intermetallics, the same empty crucible was used to create baselines under the same testing conditions at three temperatures respectively so as to minimize the equipment measurement errors. It was assumed that oxide forms

uniformly on the entire surface; therefore, the sum of all the six surface areas was used to normalize the weight gain values. For comparison, oxidation of pure Al (99.99%) was also included.

3.2.8 X-ray Photoelectron Spectroscopy (XPS)

XPS was operated in two different modes, shallow surface scan and depth profiling, in order to thoroughly examine the chemical state changes of the elements as the oxide grows and thickens on the surface of solid intermetallics during oxidation. The XPS surface measurement was performed in a Kratos AXIS Ultra spectrometer with a monochromatized Al K_{α} X-ray source (1486.71 eV) operated at a reduced power of 150 W (15 kV and 10 mA). The base pressure in the analysis chamber was 2.66×10^{-7} Pa. The core-level spectra were obtained in Al 2p and Au 4f regions at a photoelectron take-off angle of 90° measured with respect to the sample surface and were recorded in 0.1 eV step with a pass energy of 40 eV. The binding energy (b.e.) scale of the XPS spectrum was calibrated with the C 1s peak (neutral C-C peak at 284.5 eV). The chemical states for depth profiles (etching profiles) were analyzed on the same equipment for the 24 hour oxidized samples. An Ar^{+} ion gun with acceleration voltage of 4 kV and filament current of 15 mA was used to etch the samples at a gas pressure of 6.65×10^{-6} Pa. Ion bombardment was performed at an incident angle of 45° to the surface normal. The Al 2p and Au 4f spectra were obtained after each etching cycle of 3 min. Depth profiling was done until the oxygen peak became minimal. These experimental conditions in depth profiling were kept constant for all intermetallics.

Deconvolution of the experimental peak was done using CasaXPS software (Version 2.3.10). Each spectrum was fitted using a reasonable number of Gaussian-Lorentzian

curves, the shape of which could be adjusted by changing the Gaussian-Lorentzian factor in the quantification parameters list. A good fit could be achieved after a series of attempts to optimize the location and shape of the fitting curves. The positions of the resultant fitting components were automatically recorded in the quantification list. It is always possible to include as many fitting components as possible to generate a good deconvolution. However, only those components which are chemically meaningful should be considered correct. Reported values for XPS peak positions are helpful to justify a fitting component, but care should always be exercised when dealing with a material which has not been examined previously.

Chapter 4 Interface Transformations in Thin

Film Al-Au Diffusion Couples

This part of the work was done to clarify the types of intermetallics formed under two different Au:Al reservoir conditions and to analyze the effects of temperature and time of annealing. Extensive XRD was done to identify intermetallics first. Subsequently, selected samples were examined using TEM to confirm the XRD investigations and to determine the microstructures and the location sequences of intermetallics. Selected samples were also examined by TOF-SIMS to investigate the element distributions through the interfaces. Total intermetallic thicknesses were measured to analyze the growth rates.

4.1 0.3 μ m Al + 1 μ m Au Film Combination

The as-deposited 0.3 μ m Al + 1 μ m Au sample was subjected to XRD measurement immediately after the deposition cycle to avoid reaction at room temperature [94,95]. The pattern herein obtained doesn't clearly distinguish between the respective peaks of Au and Al as shown in Fig. 4.1. This was repeatedly encountered in subsequent XRD measurements for annealed samples too. Even a slow X-ray scan at a speed of 0.11°/min in conjunction with 10° fixed tilt angle could not differentiate between the two layers. The inability to differentiate Al and Au in the starting material could be due to the thick gold top layer that may preclude X-ray penetration to the Al layer. Besides, Au and Al diffraction peaks are closely located as evidenced in Table 4.1. Therefore, there could be

an overlap of the peaks of both elements. Although aluminum could not be conclusively detected by XRD in the starting material, subsequent TEM investigations have confirmed its presence. It is important to note that no reaction seems to have started at this moment as no intermetallic peaks were detected in XRD.

Fig. 4.1 XRD pattern for as-deposited 0.3μm Al + 1μm Au sample

Table 4.1 X-ray diffraction peaks of Au and Al

	2θ (degree, Cu K _α)					
Au (ICSD No. 58393)	38.182	44.390	64.573	77.544	81.717	98.128
Al (ICSD No. 52611)	38.471	44.737	65.131	78.224	82.432	99.072
Indices	1 1 1	2 0 0	2 2 0	3 1 1	2 2 2	4 0 0

(a)

(b) Diffraction pattern of Au layer

(c) Diffraction pattern of Al layer

Fig. 4.2 (a) TEM bright field micrograph of as deposited 0.3μm Al + 1μm Au sample and (b), (c) diffraction patterns of Au and Al layers

Table 4.2 Interplanar spacing of crystallographic planes in Au and Al

Au	Plane Index	2 0 0	2 2 0
	Calculated Spacing (Å)	2.012	1.407
	ICSD Data (Å)	2.039	1.442
Al	Plane Index	2 0 0	2 2 0
	Calculated Spacing (Å)	1.987	1.401
	ICSD Data (Å)	2.024	1.431

Fig. 4.3 FESEM micrograph of as deposited 0.3μm Al + 1μm Au sample

Cross section TEM bright field image of as-deposited sample is shown in Fig. 4.2(a), where the Au and Al layers are labeled. The SAD patterns obtained for the two layers are very similar in Figs. 4.2(b)-(c), making it difficult to differentiate between them based on the interplanar spacing values listed in Table 4.2. However, since the thicknesses of the films in Fig. 4.2(a) evidently agree with the nominal thicknesses intended for them, indexing of the patterns was done based on the locations where the patterns were

obtained.

The information gathered in TEM investigation could be carried to FESEM cross sectional micrographs. Fig. 4.3 shows the cross section of an as-deposited sample where three layers are clearly visible. Comparing with Fig. 4.2(a), we can identify these layers as labeled in Fig. 4.3.

Heating at elevated temperatures, 125°C, 150°C and 175°C, arouses reaction between Al and Au shortly and multiple intermetallic phases are detected in XRD measurements. The XRD patterns at each temperature are shown in Fig. 4.4(a), (b) and (c) respectively. A summary of the phases detected at the three temperatures is tabulated in Table 4.3. It can be seen that increasing temperature from 125°C to 175°C does not seem to have significantly changed the type of phases formed and sequence of formation, but only has shortened the time required for a phase to appear. This could be attributed to the increased diffusion of the elements.

Since the phase formation sequence is not affected by the temperature, the evolution of the intermetallic layers is discussed at 150°C only. A sequence of FESEM micrographs shown in Fig. 4.5 demonstrate the intermetallic formation pictorially.

(a) 125°C annealed

(b) 150°C annealed

(c) 175°C annealed

Fig. 4.4 XRD patterns for 0.3um Al + 1um Au samples annealed at three temperatures

Only Au peaks were evident in the as-deposited and 15mins annealed samples. After 15 min of annealing at 150°C, no detectable reactions took place as confirmed by the XRD pattern in Fig. 4.4(b) and the FESEM micrograph of Fig. 4.5(a). This might be an incubation period for nucleation of the new phase. After 30 min, a minor peak appeared at $2\theta = 40.40^\circ$ besides the major peak of Au at $2\theta = 38^\circ$. This early phase formation was well captured in Fig. 4.5(b) where an intermediate layer can be seen between the thick Au top layer and a thin underlayer of Al. It is not possible to identify the intermetallic merely by using this minor peak because several Al-Au intermetallics have diffraction peaks around this 2θ value. With increase in exposure time, the intermediate layer thickened giving rise to multiple new peaks in the 1h XRD pattern, all of which could be indexed to the Al_2Au_5 phase (ICSD File No. 57502). After 2 hours, Au peak intensity was seen to diminish while the intermetallic layer grew substantially to give stronger peaks. The second intermetallic phase, AlAu_4 (ICSD File No. 104616), became detectable in the 2h sample. Fig. 4.5(c) shows the two intermetallic layers between the top Au layer and the substrate. Al was probably fully consumed by this time. After 4 hours, AlAu_4 grew to give peaks with intensity nearly equivalent to those of Au peaks as demonstrated by the intensities of its three characteristic peaks. The thickening of one intermetallic layer was evidently noticeable in FESEM cross section shown in Fig. 4.5(d). Subsequently, coexistence of AlAu_4 and Al_2Au_5 was established till the end of measurements. Au probably existed in trace amount, showing some small peaks. No further transformation could be observed after 8h annealing as evidenced in Figs. 4.5(e)-(g) where two intermetallic layers of nearly equal thickness of about $0.7\mu\text{m}$ can be differentiated.

(a) 15min annealing at 150°C

(b) 30min annealing at 150°C

(c) 2h annealing at 150°C

(d) 4h annealing at 150°C

(e) 8h annealing at 150°C

(f) 16h annealing at 150°C

(g) 24h annealing at 150°C

Fig. 4.5 FESEM micrographs at various sampling times showing intermetallic compounds (IMC) evolution of 0.3 μm Al + 1 μm Au samples at 150°C

Table 4.3 List of interface transformations determined in the 0.3 μm Al + 1 μm Au samples

	0.3 μm Al + 1 μm Au		
	125°C	150°C	175°C
0 min	Au+Al	Au+Al	Au+Al
15 min	Au+Al	Au+Al	Au+Al ₂ Au ₅ +Al
30 min	Au+Al	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅
1 h	Au+Al ₂ Au ₅ +Al	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅
2 h	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅
4 h	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅
8 h	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅
16 h	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅
24 h	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅	Au+AlAu ₄ +Al ₂ Au ₅

For further confirmation of the two intermetallic compound layers obtained in the annealed samples, TEM cross section investigations were conducted on the sample annealed at 150°C for 4h. Fig. 4.6(a) shows the bright field image of this sample. Three layers marked I, II and III can be clearly distinguished in this figure. Layer I, next to the substrate, consists of columnar crystals which implies that it has undergone significant growth since its formation. The smaller thickness and crystals of Layer II probably indicates it is younger than Layer I. Layer III, unlike the other two, consists of many layers of fine crystals. Selected area diffraction (SAD) patterns were taken at positions marked as 1 to 4 in each layer and the patterns are shown in Figs. 4.6(b)–(e). Indexing of these patterns confirms that Layer I is Al_2Au_5 (trigonal, R-3cH), Layer II is AlAu_4 (cubic, P213) and Layer III is Au. Table 4.4 shows the calculated interplanar spacing of the indexed planes in each pattern and the values from the ICSD data files. These observations, while being in agreement with the x-ray diffraction results, also prove that the two intermetallics are layered sequentially in accordance with the expectation from the Al-Au equilibrium diagram.

As the samples of this set have an excess of Au, dominance of Au-rich phases is expected on prolonged annealing at high temperatures. If there is infinite supply of Au, as in actual wirebonds, AlAu_4 could be expected to be the only stable phase in the system after long anneals, along with any remnant Au. The reason for the persistence of Al_2Au_5 in this set is because the prevailing Au:Al molar ratio of 3.27:1.0 is inadequate in Au to convert it all to AlAu_4 .

(a)

(b) SAD pattern of Al₂Au₅ at Location 1

(c) SAD pattern of AlAu₄ at Location 2

(d) SAD pattern of AlAu₄ at Location 3

(e) SAD pattern of Au at Location 4

Fig. 4.6 (a) TEM bright field micrograph of 0.3 μ m Al + 1 μ m Au thin film sample annealed at 150°C for 4h and (b)-(e) diffraction patterns at locations 1,2,3,4

Investigations of the element diffusion and distribution during phase transformation were conducted using the negative ion mass SIMS depth profiling. Spectra obtained for selected samples annealed at 150°C for various times are shown in Figs. 4.7(a)-(f). The depth values indicated in the figures were computed assuming a constant sputter rate and hence may not be very accurate. However, the O profile clearly demarcates the initial Al/Au and Al/SiO₂ interfaces by two maxima at arrowed positions as shown in Fig. 4.7(a). The spacing between the two maxima is approximately 0.3 μ m which is indicative of the initial Al layer thickness. The peak at an approximate depth of 0.7 μ m is attributed to the Al/Au interface which might be caused by adsorbed oxygen atoms on the Al surface during sputtering cycles despite no discernible oxide layer being present in TEM and FESEM cross sections. With annealing, the first O peak moves to the left through Figs. 4.7(b)-(f) while the second peak is almost stationary at an approximate depth of 1.1 μ m. This signifies the migration of the initial Al/Au interface towards Au indicating that there is a net positive flux of Au into the Al film. Hence, these SIMS results prove that Au is the predominant diffusant in this system although Al diffusion in the reverse direction

should also be occurring. As intermetallics are formed between the two O peaks, the Au profile that is flat up to the SiO₂ layer decreases sharply from the position indicated by the dotted arrow in Fig. 4.7(c). Thus, the positions of the interface with the substrate indicated by both O and Au peaks are in agreement.

Table 4.4 Interplanar spacing of crystallographic planes in Au, AlAu₄ and Al₂Au₅

Au	Plane Index	-1 1 -1	-2 0 0	-1 -1 1		
	Calculated Spacing (Å)	2.254	1.963	2.215		
	ICSD Data (Å)	2.355	2.039	2.355		
AlAu ₄	Plane Index	0 1 0	0 1 1	0 0 1	1 1 -1	1 2 0
	Calculated Spacing (Å)	6.889	4.796	6.842	3.915	2.969
	ICSD Data (Å)	6.922	4.895	6.922	3.996	3.095
Al ₂ Au ₅	Plane Index	0 1 2	0 0 6	0 1 -4		
	Calculated Spacing (Å)	6.248	6.956	5.537		
	ICSD Data (Å)	6.375	7.014	5.645

(a) As deposited 0.3μm Al + 1μm Au sample

(b) 30 min annealing at 150°C

(c) 2h annealing at 150°C

(d) 4h annealing at 150°C

(e) 16h annealing at 150°C

(f) 24h annealing at 150°C

Fig. 4.7 Negative ion mass SIMS depth profiling spectra of 0.3μm Al + 1μm Au thin film samples annealed at 150°C for various times

4.2 1 μ m Al + 1 μ m Au Film Combination

A typical TEM micrograph of the cross section of the as-deposited sample is shown in Fig. 4.8. It is clear that both Al and Au layers are approximately 1 μ m thick as required and no reaction seems to have occurred at the interface. FESEM cross section of the as-deposited sample in Fig. 4.9 shows the similar results.

Fig. 4.8 TEM bright field micrograph of as deposited 1 μ m Al + 1 μ m Au sample

Fig. 4.9 FESEM micrograph of as deposited 1 μm Al + 1 μm Au sample

Thermally treated and as-deposited samples were investigated by XRD and the phases formed were identified. The x-ray diffractograms obtained at all temperatures are displayed in Fig. 4.10(a), (b) and (c) respectively. Table 4.5 summarizes all the phases that appeared at the three temperatures. It can be seen that annealing generates similar types of intermetallic phases and similar sequence of formation at all temperatures. However, the time required for a new phase to form is shortened upon increasing the temperature. Thus, only FESEM micrographs of each annealing time at 150°C are laid out in Figs. 4.11(a)-(f) as the illustration of the phase evolution.

(a) 125°C annealed

(b) 150°C annealed

(c) 175°C annealed

Fig. 4.10 XRD patterns for 1μm Al + 1μm Au samples annealed at three temperatures

Fig. 4.10(b) shows that the intermetallic formation is evident even in the first annealed sample of 15 min at 150°C as indicated by a minor peak at $2\theta = 40.48^\circ$ in the XRD pattern, but it was difficult to positively identify this new phase until it was thick enough to generate more peaks. This early phase formation was well captured by FESEM as shown in Fig. 4.11(a) where a thin intermediate layer has appeared at the Al/Au interface. In 30 min however, multiple new peaks appeared which permitted its identification as Al_2Au_5 . In the 1 h diffractogram, a few peaks attributable to AlAu_4 could be detected while Al_2Au_5 continued to grow. After 2 h anneal, Al_2Au_5 has undergone substantial growth to give peak intensities comparable to those of Au. The AlAu_4 phase also grew but its peak intensities were not as high as those of Al_2Au_5 . Cross sectional FESEM however could not differentiate between the Al_2Au_5 and AlAu_4 layers as evident in Figs. 4.11(b)-(c). Annealing for 4 h was sufficient to completely consume the Au layer as signified by the absence of Au peaks for long duration anneals. It is noteworthy that AlAu_4 peaks started to rapidly diminish while the third intermetallic of AlAu_2 (ICSD File No. 57497) began to form. The most prominent peak in the 4 hrs sample at $2\theta = 40.58^\circ$ could be a combined peak of AlAu_2 at $2\theta = 40.81^\circ$ and that of Al_2Au_5 at $2\theta = 40.45^\circ$. For annealing times higher than 4 hrs it is clear that Al_2Au_5 was being converted to AlAu_2 and ultimately the latter became the main intermetallic phase in the system. Figs. 4.11(d)-(f) show FESEM micrographs after 8, 16 and 24 h of anneal respectively where Au is absent and a thick intermetallic layer of about 1.5 μm is on top of 0.4 μm unreacted Al. The Al peaks were not detected possibly because of the thick overlying layers preventing x-ray penetration.

(a) 15min annealing at 150°C

(b) 1h annealing at 150°C

(c) 2h annealing at 150°C

(d) 8h annealing at 150°C

(e) 16h annealing at 150°C

(f) 24h annealing at 150°C

Fig. 4.11 FESEM micrographs at various sampling times showing intermetallic compounds evolution of 1 μ m Al + 1 μ m Au samples at 150°C

Table 4.5 List of interface transformations determined in the 1 μm Al + 1 μm Au samples

	1 μm Al + 1 μm Au		
	125°C	150°C	175°C
0 min	Au+Al	Au+Al	Au+Al
15 min	Au+Al ₂ Au ₅ +Al	Au+Al ₂ Au ₅ +Al	Au+Al ₂ Au ₅ +Al
30 min	Au+Al ₂ Au ₅ +Al	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅ +Al
1 h	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅ +Al	AlAu ₄ +Al ₂ Au ₅ +AlAu ₂ +Al
2 h	Au+Al ₂ Au ₅ +Al	Au+AlAu ₄ +Al ₂ Au ₅ +Al	Al ₂ Au ₅ +AlAu ₂ +Al
4 h	Au+Al ₂ Au ₅ +Al	AlAu ₄ +Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al
8 h	Au+AlAu ₄ +Al ₂ Au ₅ +Al	Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al
16 h	AlAu ₄ +Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al
24 h	Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al	Al ₂ Au ₅ +AlAu ₂ +Al

A cross section TEM bright field image is shown in Fig. 4.12(a) for a sample annealed at 150°C for 1h. Three layers can be identified besides the Al layer. Indexing of the SAD patterns in Figs. 4.12(b)-(c), obtained at locations 1 and 2 in layers I and II, unveils that they are Au and AlAu₄ respectively. The layer III was too thick for electron diffraction, but from the XRD data and the positive identification of layers I and II, it could be inferred that layer III must be Al₂Au₅. AlAu₄ seems rather thin, about 100 nm thick, suggesting it is in its early stage of growth. Table 4.6 shows the calculated interplanar spacing of the indexed planes in each pattern and the corresponding values from the ICSD data files.

(a)

(b) SAD pattern of Au at Location 1

(c) SAD pattern of AlAu₄ at Location 2

Fig. 4.12 (a) TEM bright field micrograph of 1 μm Al + 1 μm Au thin film sample annealed at 150°C for 1h and (b),(c) diffraction patterns at locations 1,2

Table 4.6 Interplanar spacing of crystallographic planes in Au and AlAu₄

Au	Plane Index	1 -1 -1	3 -1 1	2 0 2
	Calculated Spacing (Å)	2.305	1.206	1.437
	ICSD Data (Å)	2.355	1.230	1.442
AlAu ₄	Plane Index	1 3 0	1 2 1	0 1 -1
	Calculated Spacing (Å)	2.127	2.807	4.836
	ICSD Data (Å)	2.189	2.825	4.894

Fig. 4.13(a) illustrates a TEM bright field image of a sample annealed at 150°C for 4 hours. Three intermetallic layers can be observed as marked in the figure besides the residual Al layer. The SAD patterns in Figs. 4.13(b)-(d) prove that the layers are AlAu₄, Al₂Au₅ and AlAu₂ (orthorhombic, Pnnm) at locations 1, 2 and 3 respectively. At this stage, the X-ray diffractogram indicates a rapid growth of AlAu₂ with a moderate, existing amount of Al₂Au₅ and a depleting layer of AlAu₄. This is in agreement with the TEM micrograph where the AlAu₂ layer (Layer III) is getting thicker than Al₂Au₅ (Layer II). Note that Au is absent exposing the AlAu₄ (Layer I) to the atmosphere. The calculated interplanar spacing of the indexed planes in each pattern and the corresponding values from the ICSD data files are compared in Table 4.7.

(a)

(b) SAD pattern of AlAu_4 at Location 1

(c) SAD pattern of Al_2Au_5 at Location 2

(d) SAD pattern of AlAu₂ at Location 3Fig. 4.13 (a) TEM bright field micrograph of 1 μ m Al + 1 μ m Au thin film sample annealed at 150°C for 4h and (b), (c), (d) diffraction patterns at locations 1,2,3Table 4.7 Interplanar spacing of crystallographic planes in AlAu₄, Al₂Au₅ and AlAu₂

AlAu ₄	Plane Index	0 1 0	1 1 -2	1 0 -2
	Calculated Spacing (Å)	6.854	2.802	2.937
	ICSD Data (Å)	6.921	2.825	3.095
Al ₂ Au ₅	Plane Index	-1 0 2	1 -3 7	2 -3 5
	Calculated Spacing (Å)	6.314	2.251	2.402
	ICSD Data (Å)	6.375	2.331	2.421
AlAu ₂	Plane Index	2 0 0	1 7 1	-1 7 1
	Calculated Spacing (Å)	4.338	1.806	1.883
	ICSD Data (Å)	4.400	1.878	1.878

(a)

(b) SAD pattern of Al_2Au_5 at Location 1

(c) SAD pattern of AlAu_2 at Location 2

Fig. 4.14 (a) TEM bright field micrograph of $1\mu\text{m Al} + 1\mu\text{m Au}$ thin film sample annealed at 150°C for 16h and (b), (c) diffraction patterns at locations 1,2

After a long anneal of 16 hours at 150°C, XRD investigations show that AlAu_2 should be the predominant phase in the system. The cross section TEM micrograph for a 16h annealed sample shown in Fig. 4.14(a) substantiates this XRD result, where a thick middle layer remains sandwiched between two thin layers on either side. The top thin layer I was confirmed to be Al_2Au_5 by SAD in Fig. 4.14(b) and the thick middle layer II was identified to be AlAu_2 in Fig. 4.14(c). Table 4.8 gives the calculated interplanar spacing of the indexed planes in each pattern and the values from the ICSD data files.

Table 4.8 Interplanar spacing of crystallographic planes in Al_2Au_5 and AlAu_2

Al_2Au_5	Plane Index	1 0 7	1 -1 2	0 1 5
	Calculated Spacing (Å)	4.403	6.333	5.140
	ICSD Data (Å)	4.471	6.375	5.237
AlAu_2	Plane Index	2 -7 0	0 0 2	2 -7 2
	Calculated Spacing (Å)	2.133	1.621	1.286
	ICSD Data (Å)	2.104	1.610	1.278

Figs. 4.15(a)-(f) show the negative ion mass SIMS depth profiling spectra for selected samples annealed at 150°C for various times. As in the case of 0.3µm Al + 1µm Au samples, the two maxima in the O profile at the arrowed positions in Fig. 4.15(a) indicate the initial Au/Al interface at approximately 0.7µm depth and Al/SiO₂ interface at 1.4µm depth. As anneal proceeds, the first O peak shifts towards the thin film surface while the other is almost stationary at about 1.4µm depth. Another interface could be identified in the Au profile after 30 min anneal. This is indicated by the dotted arrow in Fig. 4.15(b) at the point where Au concentration begins to decrease abruptly. This could be the interface between the intermetallics and remaining Al. As the Al is being consumed, this interface should move closer to the second O peak that is the interface with the substrate. After 24h

anneal, Fig. 4.15(f) shows that the first O peak has almost reached the surface signifying the full consumption of Au. The intermetallics/Al interface is apart from the second O peak by about $0.4\mu\text{m}$ which is the approximate thickness of remaining Al, as clear from the FESEM micrograph of Fig. 4.11(f). Hence, these SIMS results again prove that Au is the predominant diffusant in this system.

(a) As deposited $1\mu\text{m}$ Al + $1\mu\text{m}$ Au sample

(b) 30 min annealing at 150°C

(c) 2h annealing at 150°C

(d) 4h annealing at 150°C

(e) 16h annealing at 150°C

(f) 24h annealing at 150°C

Fig. 4.15 Negative ion mass SIMS depth profiling spectra of 1 μm Al + 1 μm Au thin film samples annealed at 150°C for various times

4.3 Discussion

4.3.1 Experimental Phase Formation Sequence

Our study in the range 125°C to 175°C, while agreeing with the general trends observed by the previous workers, has additionally shown that the intermetallics are layered with sharp boundaries, and that the grain structure within each layer changes with annealing conditions and the element molar ratio. The sequence of phases that forms for the two Au:Al molar ratios can be depicted by Figs. 4.16(a) and (b) where the time increases from left to right. In both sets of samples, Al_2Au_5 was the first phase formed at the early stage of annealing followed by AlAu_4 . The latter appeared at the interface between Au and Al_2Au_5 as expected by the phase equilibrium leading to a layer structured interface. In the

1 μm Al + 1 μm Au structure, however, AlAu₂ appeared at a later stage while AlAu₄ declined and finally disappeared.

Fig. 4.16 Intermetallic phase transformation diagram of (a) 0.3 μm Al + 1 μm Au and (b) 1 μm Al + 1 μm Au samples in the range from 125°C to 175°C

The structure of 0.3 μm Al + 1 μm Au was intentionally designed to simulate the scenario in wire bonds where Au is in excess. Breach and Wulff [71] reported the formation of Al₂Au₅ as the initial intermetallic phase in wire bonds annealed at 175°C, followed by AlAu₄ at the interface between Al₂Au₅ and Au ball. They found Al metallization under the ball to be completely consumed. The intermetallic phases and their formation sequence identified in the present study agree with these results. AlAu₂ was also found by Breach and Wulff [71] at the periphery of the wire bonds, which was assisted by extra supply of Al from the metallization layer outside the ball to react with Al₂Au₅. Since there is no such additional supply of Al in present study, AlAu₂ was not observed. An approximate mass balance calculation could be made using the nominal initial Al and Au thicknesses, along with the respective theoretical densities in g·cm⁻³ of Al₂Au₅ = 15.23,

$\text{AlAu}_4 = 16.38$, $\text{Al} = 2.70$ and $\text{Au} = 19.3$. The thicknesses of Al and Au needed to form the two layers of Al_2Au_5 and AlAu_4 of about $0.7\mu\text{m}$ in Fig. 4.5(g) are calculated to be $0.31\mu\text{m}$ and $1.02\mu\text{m}$ respectively, approximately equal to the initial layer thicknesses. Hence, the experimentally measured thicknesses of individual layers are in good agreement with mass balance calculation.

As for the $1\mu\text{m Al} + 1\mu\text{m Au}$ structure, reports in the literature indicate the coexistence of Al_2Au and AlAu_2 after prolonged anneals [19] [31] and, finally AlAu is formed as the end product in couples with Al and Au of equivalent thicknesses. Al_2Au or AlAu were not detected up to 24 hrs of anneal even at the highest temperature of 175°C in the present study. Al and Au films of equal thickness contain nearly the same number of aluminum and gold atoms per unit area, a factor which favors the formation of AlAu from a stoichiometry perspective. The reason for not forming AlAu in our system might be attributed to the formation of AlAu_4 . AlAu_4 , although a transient phase, removes and binds Au atoms from the diffusion flux, thus hindering the formation of Al_2Au , the compound with low Au content near the Al layer. Since Al_2Au is reportedly a necessary precursor for AlAu formation [19], formation of the latter is prevented. Taking the theoretical densities of AlAu_2 ($14.42\text{ g}\cdot\text{cm}^{-3}$) and Al, the layer of nearly $1.5\mu\text{m}$ AlAu_2 on top of $0.4\mu\text{m}$ unreacted Al after 24 h anneal in Fig. 4.11(f) is found to comply with the mass balance principle. The remaining Al could possibly convert AlAu_2 into AlAu to achieve final equilibrium given enough time and/or appropriate temperature.

4.3.2 Theoretical Prediction of Phase Formation Sequence

The formation of Al_2Au_5 as the initial interface intermetallic is in agreement with previous studies dealing with both thin film couples and wire bonds. Al_2Au_5 was

normally found to have the largest thickness during annealing as reported by Philofsky [29] and Noolu [10]. Table 4.9 summarizes the interdiffusion coefficients in Al_2Au_5 , AlAu_2 and AlAu_4 at three temperatures. It can be seen that the interdiffusion coefficient in Al_2Au_5 is one order of magnitude higher than that in AlAu_2 and AlAu_4 , a factor that agrees with the “first phase, fast phase” theory [37]. However, according to Table 4.9, this theory also implies that AlAu_2 should form as the second phase as it has a higher interdiffusion coefficient than that of AlAu_4 , but this is not observed in our work. This theory seems insufficient to explain the formation of second phase in the present study.

Table 4.9 Interdiffusion coefficients of AlAu_2 , Al_2Au_5 and AlAu_4 [10]

	$D_{\text{interdiffusion}} \text{ (m}^2\text{/sec)}$		
	AlAu_2	Al_2Au_5	AlAu_4
125°C	9.198×10^{-19}	5.393×10^{-18}	7.238×10^{-20}
150°C	2.580×10^{-18}	2.115×10^{-17}	2.895×10^{-19}
175°C	6.448×10^{-18}	7.121×10^{-17}	9.917×10^{-19}

Formation of AlAu_4 as the second phase was not reported except in situations with very low Al contents. Our work shows that AlAu_4 was formed as the second phase even under nearly equal amounts of Au and Al. Pretorius [43,44] calculated the effective heats of formation of Al_2Au_5 ($\Delta H = -20$ kJ/mol) and AlAu_2 ($\Delta H = -19.8$ kJ/mol) assuming an effective interface concentration of 78 at.% Au corresponding to the lowest liquidus temperature. As the values are very close to each other, either could form as the first intermetallic phase depending on the experimental conditions. Formation of Al_2Au_5 seems more favorable in our study. The heat of formation of AlAu_4 ($\Delta H = -18.5$ kJ/mol) was reportedly higher and therefore it would not appear prior to Al_2Au_5 . But since the composition of AlAu_4 (80 at.% Au) is closer to the effective interface concentration of 78

at.% than that of AlAu₂ (67 at.% Au), AlAu₄ is likely to be formed prior to AlAu₂ as the effective concentrations at the two interfaces of Al₂Au₅ shift. The sequence of transformations observed in our study proves this prediction. However, heat of formation is not the only criterion that determines interface reactions, nucleation and growth kinetics considerations may also dictate the sequence.

Table 4.10 Heats of formation (ΔH°) of the Al-Au intermetallics [43]

	Al ₂ Au	AlAu	AlAu ₂	Al ₂ Au ₅	AlAu ₄
ΔH° (298K) (kJ/mol)	-31	-37	-30	-26	-19

According to the nucleation suppression theory by Gusak [42], the heats of formation of the five Al-Au intermetallics as shown in Table 4.10 can be used to approximate their respective Gibbs free energy of formation, and to evaluate the nucleation suppression for the second phase. In our study, the second phase could be either AlAu₄ or AlAu₂. With Al₂Au₅ being the existing intermetallic, the driving force diagram for AlAu₄ and AlAu₂ can be constructed as shown in Fig. 4.17, from which the driving force, $\Delta g_{20}^{\text{AlAu}_4}$, of reaction at Al₂Au₅/Au interface

can be calculated to be -0.82 kJ/mol. Applying the nucleation suppression criterion as expressed in Equation (2.1) produces

$$\frac{\Delta x_1^{\text{AlAu}_4}}{l_1^{cr}} < 5 \frac{C_2 - C_1}{C_1(1 - C_1)} \left(\frac{\Delta g_{10}}{\Delta g_{20}^{\text{AlAu}_4}} \right)^2 \approx 423$$

where $\Delta x_1^{\text{AlAu}_4}$ is the critical size of Al₂Au₅ required for nucleation of AlAu₄, $C_2 = 4/5$, $C_1 = 5/7$, $\Delta g_{10} = -26$ kJ/mol, l_1^{cr} is the standard critical size of Al₂Au₅ nucleus.

Fig. 4.17 Driving forces for the formation of AlAu₂ and AlAu₄ as the second intermetallic

Similarly, the driving force, $\Delta g_{20}^{\text{AlAu}_2}$, of the reaction at the Al/Al₂Au₅ interface

is calculated to be -5.72 kJ/mol. Thus the critical size of Al₂Au₅ required for nucleation of AlAu₂, $\Delta x_1^{\text{AlAu}_2}$, can be obtained according to the nucleation suppression condition as

$$\frac{\Delta x_1^{\text{AlAu}_2}}{l_1^{cr}} < 5 \frac{C_2 - C_1}{C_1(1 - C_1)} \left(\frac{\Delta g_{10}}{\Delta g_{20}^{\text{AlAu}_2}} \right)^2 \approx 5$$

where $C_2 = 1/3$, $C_1 = 2/7$. It can be noted that $\Delta x_1^{\text{AlAu}_2} \ll \Delta x_1^{\text{AlAu}_4}$, which implies that AlAu₂ should be nucleated prior to AlAu₄ when Al₂Au₅ thickens. This is contradicting our experimental results where AlAu₄ was identified to grow as the second phase. As nucleation is the initial stage of intermetallic formation, the factors that could affect the second phase formation kinetically in subsequent growth stage should also be considered.

The diffusive suppression effect proposed by Gusak [40,41] is one of the factors. Table 4.9 shows the interdiffusion coefficients in the three intermetallics are in the order of Al₂Au₅ > AlAu₂ > AlAu₄. Consequently, the diffusive suppression effect caused by the fast

growing first phase, Al_2Au_5 , on the growth of AlAu_4 shall be more significant than that for AlAu_2 , and thus AlAu_2 is supposed to grow prior to AlAu_4 . On the other hand, the influence of chemical reaction barrier, suggested by K. N. Tu [38,39], on the suppression of second phase formation is also a critical issue to be considered, but it's not possible to quantitatively evaluate its role in the formation of AlAu_2 and AlAu_4 due to lack of data such as the chemical reaction constants for reactions to form Al_2Au_5 , AlAu_2 and AlAu_4 . It appears that several factors could affect the phase formation and some even operate in opposite directions. The real phase formation should be the overall interaction of all these factors discussed.

4.3.3 Dominance of Au Diffusion

Intermetallic compound formation in binary system is indeed a process involving mutual diffusion of both elements across the layered structures. However, it is often considered, for the sake of simplicity, that the growth of such compounds is governed by the motion of only one species on the premise that diffusion generally occurs more rapidly into the lower melting point component, leading to the assumption that gold diffusion might be the dominating process in Al-Au diffusion couples. Weaver [26] and Noolu [96] applied this assumption to explain the specific phenomena in their experiments, but experimental evidence to prove the predominance of Au diffusion has yet not been sufficient. In the present study, negative ion mass SIMS depth profiling spectra for both sets reveal that Au is the dominant diffusant. Al and Au atoms are very similar in many aspects as shown in Table 4.11 below. These similarities imply that they could diffuse in the intermetallic at almost same rate. However, the intermetallics identified in this project, Al_2Au_5 , AlAu_2 and AlAu_4 , contain more Au atoms than Al atoms in their crystals. Therefore, when Au atoms diffuse in the intermetallic, there are adequate neighboring Au atoms to participate

in and sustain the diffusion process, whereas it might take longer for Al atoms to migrate in the lattice because there are less Al atoms. This might be the reason for faster diffusion of Au observed in the thin films in present study. Since thin film samples are normally polycrystalline and contain high density of defects, namely grain boundaries and vacancies within the grains [97], it could be delineated that gold atoms diffuse through these defects sites to react with aluminum. Interstitial diffusion of gold into aluminum grains is not likely to occur owing to their similar atomic radius.

Table 4.11 Comparison of atomic properties for Al and Au

	Crystal structure	Atomic radii (nm)	Lattice parameter (Å)	Atomic packing factor
Au	FCC	0.144	4.078	0.74
Al	FCC	0.143	4.056	0.74

4.3.4 Intermetallic Growth Kinetics

It is a common practice to measure the thickness of individual intermetallic layer as a function of time to generate an appropriate kinetic study for any specific phase. However, it is not always possible in our study to identify every intermetallic layer in the thin films, e.g. Al_2Au_5 and AlAu_4 could not be distinguished in the $1\mu\text{m Al} + 1\mu\text{m Au}$ samples. Therefore, the total intermetallic compound growth was used for the kinetic study and the growth curves at different temperatures are plotted in Figs. 4.18(a)-(b). According to Kidson [98], the growth of intermetallic phase during annealing should follow the parabolic rate law:

$$x = kt^{1/2}$$

where x is the thickness of intermetallic layer, t is the time and k is the rate constant. At 125°C , an overall parabolic growth curve can be observed in $1\mu\text{m Al} + 1\mu\text{m Au}$ samples,

indicating a continuous diffusion driven growth throughout the experiment duration. It is also clear that at 150°C and 175°C the thickness appears to reach an upper bound after initial growth. This could be attributed to one of the elements being consumed retarding, but not stopping, further growth. The parabolic growth equation was therefore fitted, using the parabolic equation fitting tools in Origin 7.0 software, to all the data points at 125°C and those appearing to obey it in the initial stage at 150°C and 175°C. The same feature was generally observed in 0.3µm Al + 1µm Au samples as well despite there exists an incubation period at 125°C and 150°C. Since the incubation time was short and its exact value was unknown, it was ignored when fitting the data points following the same fitting procedures. The corresponding values of k were determined and tabulated in Table 4.12.

(a)

(b)

Fig. 4.18 Overall intermetallic compound growth curves for (a) 0.3 μm Al + 1 μm Au and (b) 1 μm Al + 1 μm Au thin film couples at three temperatures

Table 4.12 Summary of overall intermetallic growth rate constants

	k ($\mu\text{m}/\text{min}^{1/2}$)		
	125°C	150°C	175°C
0.3 μm Al + 1 μm Au	0.01779±0.00065	0.04965±0.00474	0.07301±0.00396
1 μm Al + 1 μm Au	0.04634±0.00135	0.09128±0.00462	0.14318±0.01341

Fig. 4.19 demonstrates the relationship between $\ln k$ and $1/T$ for both structures, from which the Arrhenius-type equations of k could be fitted as follows:

$$0.3 \mu\text{m Al: } k = 6794.17 \times \exp\left(\frac{-42.298 \pm 4.652 \text{ kJ/mol}}{RT}\right) \mu\text{m} / \text{min}^{1/2}$$

$$1 \mu\text{m Al: } k = 1205.84 \times \exp\left(\frac{-33.602 \pm 2.519 \text{ kJ/mol}}{RT}\right) \mu\text{m} / \text{min}^{1/2}$$

Philofsky [29] established the expression of k as below when there is adequate supply of both Al and Au in temperature range 200°C to 460°C:

$$k = 1766.35 \times \exp\left(\frac{-33.262 \text{ kJ/mol}}{RT}\right) \mu\text{m} / \text{min}^{1/2}$$

The present study agrees very well with Philofsky's results for 1 μm Al + 1 μm Au samples despite being at a lower temperature range. This could be due to the fact that Al and Au are in equivalent supply in our study, similar to Philofsky's condition. The activation energy could not be the same for 0.3 μm Al + 1 μm Au samples as the intermetallics formed are different even though the predominant diffusant is still Au. Noolu [10] reported the activation energies of growth rate constants in kJ/mol of Al_2Au_5 =38.1, AlAu_4 =38.7 and AlAu_2 =28.9. The activation energies herein obtained are close to the values of Al_2Au_5 and AlAu_4 , probably because the parabolic fitting was basically made to the periods of annealing when Al_2Au_5 and AlAu_4 are predominantly present in the thin films. Since the initial growth of AlAu_2 also starts in some of the fitting points of 1 μm Al + 1 μm Au samples, the activation energy for this set is relatively lower. Moreover, none of the activation energies obtained should be mistaken as that of any individual intermetallic phase, it is an integrated value for several processes such as diffusion, chemical reaction and phase transformation.

Fig. 4.19 The Arrhenius plots for growth rate constant k in thin film couples

4.4 Conclusions

The following conclusions can be drawn from the investigations conducted in thin film diffusion couples of $0.3\mu\text{m Al} + 1\mu\text{m Au}$ and $1\mu\text{m Al} + 1\mu\text{m Au}$ for interface reactions up to 24-hour isothermal anneals at 125°C , 150°C and 175°C .

1. Al_2Au_5 was the first intermetallic to be detected at the Al-Au interface followed by AlAu_4 in all samples. In $1\mu\text{m Al} + 1\mu\text{m Au}$ samples, however, AlAu_4 was only a transient phase and AlAu_2 formed as the third intermetallic.
2. After prolonged anneal, the predominant intermetallic in $0.3\mu\text{m Al} + 1\mu\text{m Au}$ structure was AlAu_4 , and in $1\mu\text{m Al} + 1\mu\text{m Au}$ was AlAu_2 .

3. The intermetallics were layered with sharp boundaries in accordance with predictions from equilibrium diagram.
4. The O peak observed in the SIMS analysis at the initial Al/Au interface could be used as an interface marker. Its migration towards the Au layer shows that there is a net Au atom diffusion into Al.
5. The growth kinetics of the intermetallics obey parabolic growth law at 125°C for both structures. At 150°C and 175°C, the parabolic law appears to be obeyed only in the early stages. Subsequently, when either Au or Al is fully consumed, the growth stalls but phase transformations continue towards the intermetallic phase that is thermodynamically most stable under the conditions.
6. The Arrhenius relationships were determined for the parabolic growth rate constants, which show that the activation energy for interface intermetallic growth is 42.298 kJ/mol for 0.3µm Al + 1µm Au structure and 33.602 kJ/mol for 1µm Al + 1µm Au.

Chapter 5 Moving Boundary Model for Intermetallic Growth

The growth of intermetallic compound (IMC) has been found to impose a compound effect on the reliability control for wire bonding. A layer of intermetallics of appropriate thickness is essentially needed to give mechanical strength, yet too much intermetallic growth will lead to brittle fractures at the interface. While a number of physical models based on diffusion laws have been proposed to predict the growth of intermetallics, a common feature is that they utilized a number of immeasurable values [99 – 101], which makes them more like the curve-fitting methods rather than computational ones. Moreover, some computational models derived from the phase lag effect possess a deficiency, which might lead to misunderstanding, either with the setting of the coordinate system or the prescription of the boundary conditions [102–105]. In this chapter, an explicit numerical front-tracking algorithm of the moving boundary problem is utilized to predict the early intermetallic growth in Al-Au diffusion couple. The stability of this algorithm is studied in detail. The finding of Au as the main diffusant in the preceding chapter justifies the simplified treatment of interdiffusion as unilateral diffusion of Au, and the experimental data obtained therein provide a measure of the validity of the numerical algorithm.

5.1 Model for IMC Growth Controlled by Diffusion

The model considers bulk diffusion between two contacting materials, Al and Au, and

assumes that only one intermetallic phase, Al_2Au_5 , is formed. The formation of IMC starts at the interface between the two metals. Meanwhile, since Au has been found to be the main diffusant, the interdiffusion process is deemed as a one-way diffusion of Au into IMC followed by the chemical reaction with Al atoms at the interface between IMC and Al as schematically shown in Fig. 5.1.

Fig. 5.1 Schematic illustration of modeling assumption

The molar concentration of Au in IMC could be given by the Fick's law:

$$\frac{\partial C_{Au}}{\partial t} = D \frac{\partial^2 C_{Au}}{\partial x^2} \quad (0 < x < l) \quad (5.1)$$

where D is the diffusivity of Au in IMC and l the thickness of IMC. D is assumed to be independent of concentration.

The initial condition for the present problem is:

$$C_{Au}(x, 0) = 0 \text{ when } x > 0,$$

which implies that the Au and Al layers are initially separated by a sharp interface and no intermixing occurs at this stage. The boundary conditions for the intermetallic layer are:

Left side: $C_{Au}(0, t) = C_0$ where $x=0$

Right side: $C_{Au}(l, t) = 0$ where $x=l$

Obviously, it is assumed there is a constant supply of Au and the concentration discontinuity across the boundaries is ignored herein for the simplicity of mathematic treatment. Using the mass continuity condition in a control volume at the IMC/Al interface, the growth rate of the IMC layer can be expressed as:

$$Au \text{ wt}\% \times \rho_{Al_2Au_5} \times \frac{dl}{dt} = -m_0 D \left. \frac{\partial C_{Au}}{\partial x} \right|_{x=l} \quad (5.2)$$

where m_0 is the molar mass of Au, $Au \text{ wt} \%$ the weight percentage of Au in Al_2Au_5 , $\rho_{Al_2Au_5}$ the density of Al_2Au_5 .

5.2 Dimensionless Form of Equations

For the convenience in numerical simulation, partial differential equations are usually translated into dimensionless forms. In the present model, the variables in Equations (5.1) and (5.2) can be transformed into the following dimensionless variables:

$$X = \frac{x}{L} \quad T = \frac{Dt}{L^2} \quad C = \frac{C_{Au}}{C_0} \quad S = \frac{l}{L}$$

where: L is the entire thickness of the diffusion range, i.e. the thickness of Al, C_0 the molar concentration of Au at the Au side.

Equations (5.1) and (5.2) in the new dimensionless forms become:

$$\frac{\partial C}{\partial T} = \frac{\partial^2 C}{\partial X^2} \quad (0 < X < S) \quad (5.3)$$

$$\lambda \frac{dS}{dT} = - \left. \frac{\partial C}{\partial X} \right|_{X=S} \quad (5.4)$$

where: $\lambda = \frac{Au \text{ wt}\% \times \rho_{Al_2Au_5}}{m_0 C_0}$. The next step is to formulate an appropriate numerical scheme to solve these dimensionless equations.

5.3 Front-Tracking Numerical Algorithm

5.3.1 Illustration of Algorithm

Assuming the entire thickness of Al is subdivided into N intervals with equal width $dX=1/N$, the position of each space grid is $X_n = n dX$, $n = 0, 1, 2 \dots N$. We intend to calculate the concentration of Au at each space grid n at the time level $j+1 dT$, $C_{n,j+1}$, by use of the concentration values, $C_{n,j}$, at the preceding time level $j dT$. At any moment $j dT$, the moving boundary of IMC lies between the i th and $i+1$ th grids with a fraction p_j from the i th grid ($0 < p_j < 1$). Therefore, the location of boundary at $j dT$ level can be represented as: $S_j = (i + p_j) dX$ as depicted in Fig. 5.2.

Fig. 5.2 The location of moving boundary at $j dT$ time level

5.3.2 Discretization of Equations

The Lagrange interpolation method where any continuous function can be approximated by 3-point interpolation is [106 –108]:

$$f(x) = \frac{(x-a_1)(x-a_2)}{(a_0-a_1)(a_0-a_2)} f(a_0) + \frac{(x-a_0)(x-a_2)}{(a_1-a_0)(a_1-a_2)} f(a_1) + \frac{(x-a_0)(x-a_1)}{(a_2-a_0)(a_2-a_1)} f(a_2)$$

where a_0, a_1, a_2 are three continuous points. Further, the derivatives of function $f(x)$ can be obtained as:

$$f'(x) = \frac{2x-a_1-a_2}{(a_0-a_1)(a_0-a_2)} f(a_0) + \frac{2x-a_0-a_2}{(a_1-a_0)(a_1-a_2)} f(a_1) + \frac{2x-a_0-a_1}{(a_2-a_0)(a_2-a_1)} f(a_2) \quad (5.5)$$

$$f''(x) = \frac{2}{(a_0-a_1)(a_0-a_2)} f(a_0) + \frac{2}{(a_1-a_0)(a_1-a_2)} f(a_1) + \frac{2}{(a_2-a_0)(a_2-a_1)} f(a_2) \quad (5.6)$$

Therefore at j dT time level, for any three sequential space grids in the present model, Equation (5.3) can be discretized with reference to Equation (5.6) as:

$$\frac{C_{n,j+1} - C_{n,j}}{dT} = \frac{1}{(dX)^2} (C_{n-1,j} - 2C_{n,j} + C_{n+1,j}) \quad n = 1, 2, 3, \dots, i-1 \quad (5.7)$$

As for the concentration at grid i , which is adjacent to the boundary in Fig. 5.2, grids $i-1, i$ and the boundary itself are selected as three consecutive points to build the approximation as follows:

$$\frac{C_{i,j+1} - C_{i,j}}{dT} = \frac{2}{(dX)^2} \left(\frac{C_{i-1,j}}{p_j + 1} - \frac{C_{i,j}}{p_j} \right) \quad (5.8)$$

It's seen that Equation (5.4) involves the first order of derivative at the boundary. Hence, Equation (5.5) as well as the expression $S_j = (i + p_j) dX$ yields:

$$\frac{p_{j+1} - p_j}{dT} = -\frac{1}{\lambda(dX)^2} \left(\frac{p_j C_{i-1,j}}{p_j + 1} - \frac{(p_j + 1) C_{i,j}}{p_j} \right) \quad (5.9)$$

This can be used to predict the value of p_{j+1} . Thus, the numerical simulation scheme can be structured as:

1. Calculate p_{j+1} from (5.9);

2. Calculate $C_{n,j+1}$, $n = 1, 2, 3, \dots, i-1$, from (5.7);
3. Calculate $C_{i,j+1}$ from (5.8);
4. Repeat 1~3 to calculate p_{j+2} , $C_{n,j+2}$, $C_{i,j+2}$.

5.4 Stability Study of Numerical Algorithm

The two difference equations (5.7) and (5.8) which connect the grid concentrations at two sequential time levels can be presented in the following matrix form:

$$\begin{pmatrix} C_1^{j+1} \\ C_2^{j+1} \\ C_3^{j+1} \\ \vdots \\ C_{i-1}^{j+1} \\ C_i^{j+1} \end{pmatrix} = \begin{pmatrix} 1-2r & r & & & & \\ r & 1-2r & r & & & \\ & r & 1-2r & r & & \\ & & & \ddots & & \\ & & & & r & 1-2r \\ & & & & \frac{2r}{1+p^j} & 1-\frac{2r}{p^j} \end{pmatrix} \begin{pmatrix} C_1^j \\ C_2^j \\ C_3^j \\ \vdots \\ C_{i-1}^j \\ C_i^j \end{pmatrix} + \begin{pmatrix} r \\ 0 \\ 0 \\ \vdots \\ 0 \\ 0 \end{pmatrix}$$

$$= A_j \begin{pmatrix} C_1^j \\ C_2^j \\ C_3^j \\ \vdots \\ C_{i-1}^j \\ C_i^j \end{pmatrix} + B \quad (5.10)$$

where A_j is a square matrix of order i , B is a one-column constant matrix, $r = dT/(dX)^2$. It is obvious the dimension of A_j is varying as i increases with time. Equation (5.10) can be rewritten in a short form as:

$$C^{j+1} = A^j C^j + B \quad (5.11)$$

Let ψ denotes the computed values of C , so that we actually have solved the equation:

$$\Psi^{j+1} = A^j \Psi^j + B \quad (5.12)$$

So the computational error is estimated by subtracting (5.12) from (5.11). Suppose the computational error introduced at j dT time level is presented by vector e^j , then:

$$\mathbf{C}^{j+1} - \Psi^{j+1} = \mathbf{A}^j (\mathbf{C}^j - \Psi^j) \quad (5.13)$$

i.e.

$$\mathbf{e}^{j+1} = \mathbf{A}^j \mathbf{e}^j \quad (5.14)$$

It is straightforward to deduce the following expression due to the recurrence of (5.14):

$$\mathbf{e}^{j+1} = \mathbf{A}^j \mathbf{A}^{j-1} \mathbf{A}^{j-2} \dots \mathbf{A}^2 \mathbf{A}^1 \mathbf{e}^0 = \prod_{n=1}^j \mathbf{A}_n \mathbf{e}^0 \quad (5.15)$$

where $\mathbf{e}^0$ is the error vector for the starting values.

According to the matrix theory of stability analysis [108], the series of matrices $\mathbf{A}$ in Equation (5.15) determines how the error vectors are transferred consecutively. To ensure the numerical scheme presented is stable to produce reasonable simulation results, it is required that an appropriate norm of the error vector is bounded so that the error vector will drop off as time proceeds. This can be interpreted as:

$$\left\| \prod_{n=1}^j \mathbf{A}_n \right\| \leq \prod_{n=1}^j \|\mathbf{A}_n\| \leq 1 \quad (5.16)$$

It is convenient to require that the norm of every matrix $\mathbf{A}$ in the series is less than unity, such that the above inequality will always be satisfied. Therefore, for any $\mathbf{A}$, its spectrum radius must be less than or equal to 1:

$$\rho(\mathbf{A}) \leq 1 \quad (5.17)$$

As a result, the moduli of all the eigenvalues of $\mathbf{A}$ must be within unity in order for (5.17) to be satisfied. Meanwhile, as the Brauer's theorem shows that the modulus of each eigenvalue λ of a square matrix must be confined in or on a Brauer disk, the following conditions must be satisfied for $\mathbf{A}$:

$$|\lambda - (1 - 2r)| \leq 2r \quad (5.18)$$

$$\left| \lambda - \left(1 - \frac{2r}{p^j}\right) \right| \leq \frac{2r}{1 + p^j} \quad (5.19)$$

From (5.18),

$$-4r + 1 \leq \lambda \leq 1$$

Since $|\lambda| \leq 1$

$$|-4r + 1| \leq 1$$

So that

$$r \leq \frac{1}{2} \quad (5.20)$$

From (5.19), the two bounds of λ can be found as:

$$\lambda_1 = 1 - \frac{2r}{p^j(1 + p^j)} \quad \lambda_2 = \frac{2r(1 + 2p^j)}{p^j(1 + p^j)} - 1$$

For stability, it is required;

$$-1 \leq \lambda_1 = 1 - \frac{2r}{p^j(1 + p^j)} \leq 1$$

$$-1 \leq \lambda_2 = \frac{2r(1 + 2p^j)}{p^j(1 + p^j)} - 1 \leq 1$$

In the end, it can be shown that:

$$p^j \geq r - \frac{1}{2} + \sqrt{r^2 + \frac{1}{4}} \quad (5.21)$$

Therefore, the three parameters, p_j , dT , dX , involved in the present numerical model are found to be related for the stability of the scheme. This relation must be monitored at every time step by certain code in the computational program.

5.5 Modeling Results

The prediction of intermetallic growth using the front tracking algorithm was compared with the experimental data obtained in Al-Au thin film study. The physical constants and

parameters used in modeling are listed in Table 5.1. Fig. 5.3 shows a prediction of IMC growth at 125, 150 and 175°C using 100 space grids and 155,000 time grids. The diffusion range, namely the thickness of the Al layer, was assumed to be 1µm and the diffusivities of Au in Al₂Au₅ were calculated from literature data for intermetallic growth in wire bonds. The IMC thicknesses measured in 1µm Al + 1µm Au thin films when Al₂Au₅ is identified in Table 4.5 as the single or predominant phase in the presence of an emerging AlAu₄ phase are represented by the symbols at each temperature respectively. It is clear that the parabolic prediction matches most of the experimental measurements at 125°C. At higher temperatures, the simulated curves still generally agree with the IMC growth trend despite the Al₂Au₅ dominant period is shortened. Hence, the algorithm developed herein is found to agree very well with the experiment data. If the diffusion range is changed to 0.3µm, the same algorithm could be applied to 0.3µm Al + 1µm Au samples. Fig. 5.4 shows the results of such attempts. However, it can be seen that the simulation curves significantly deviate from the experimental data, predicting a more rapid intermetallic growth than really observed in this set of samples at every temperature.

Table 5.1 Physical parameters used in modeling [10]

Parameters	Values
Diffusivity at 125°C	$1.198 \times 10^{-3} \mu\text{m}^2/\text{min}$
Diffusivity at 150°C	$4.699 \times 10^{-3} \mu\text{m}^2/\text{min}$
Diffusivity at 175°C	$1.582 \times 10^{-2} \mu\text{m}^2/\text{min}$
Density of Al ₂ Au ₅ ($\rho_{\text{Al}_2\text{Au}_5}$)	$1.5231 \times 10^{-11} \text{ g}/\mu\text{m}^3$
Weight percent of Au in Al ₂ Au ₅ (Au wt %)	95.1143%
Molar mass of gold (m₀)	196.9665 g/mol

Left side boundary condition (C_0)

$$9.7986 \times 10^{-14} \text{ mol/}\mu\text{m}^3$$

Fig. 5.3 Prediction of IMC growth assuming diffusion range of 1 μm

Fig. 5.4 Prediction of IMC growth assuming diffusion range of $0.3\mu\text{m}$

5.6 Discussion

The moving boundary front tracking algorithm developed in this chapter differs from other methods in a way that all the parameters involved are calculable and thus it enables computation of the IMC thickness, instead of curve fitting to determine some physically immeasurable factors as in other approaches which are less computational. Therefore, the validity of this algorithm highly depends on how precisely all the values are given, especially the diffusivity. The diffusivities used in this study were reported in the early investigations on wire bonds where the amounts of Al and Au are sufficient, enabling precise measurements of the thickness of each phase and the determination of the diffusivities. The prediction closely matching the experimental data of $1\mu\text{m}$ Al + $1\mu\text{m}$ Au thin film samples prove their accuracy.

The mismatch of the numerical simulation to experimental data for 0.3 μm Al + 1 μm Au samples is caused by the dimensionless conversion of the variables as shown below:

$$X = \frac{x}{L} \quad T = \frac{Dt}{L^2} \quad C = \frac{C_{Au}}{C_0} \quad S = \frac{l}{L}$$

It can be noted that the thickness of intermetallic l is converted to S after being modulated by L which is the entire thickness of Al. In our project, the thickness L differs significantly in the two thin films, being 1 μm in one case and 0.3 μm in another. This treatment transforms the two distinct situations into a uniform condition where the diffusion range is confined between 0 and 1 after conversion. However, this also implies that, for the same value of l , the resultant S can be magnified if L is initially small, and minified if L is large. This effect can be illustrated in Fig. 5.5. A relatively larger S essentially requires more time steps to compute with a given time length. This increase in time steps is not linear, thus it cannot be offset by the linear counter-conversion of S to l , ultimately resulting in a prediction of faster growth than measured. On the other hand, more time steps allow for the accumulation of more errors including truncation errors and computational errors. These could lead to the mismatch of the numerical simulation to experimental data for 0.3 μm Al + 1 μm Au samples. Therefore, the numerical model developed in this project potentially requires a relatively large diffusion length in order to work efficiently.

Fig. 5.5 Illustration of the effect of dimensionless conversion

For simplicity, the model only considers the growth of Al_2Au_5 as a result of element diffusion. This is based on the fact that Al_2Au_5 is observed in many studies as the single phase in early stage of intermetallic growth. The moving boundary model is found effective to simulate its growth in this period. The model will become erroneous when more phases begin to grow since new interfaces would appear and the interface barriers for diffusion would impact the average diffusivity of Au. To simulate a scenario where multiple intermetallics grow simultaneously, a multi-phase model is needed in which the growth or annihilation of a phase is represented by the movements of two moving boundaries with neighboring phases. It is much more complex than single-phase model because it might require the fundamental understanding of thermodynamics of nucleation and phase competition.

From thermodynamics point of view, there is a quantum change in concentration of diffusant across the boundaries, i.e. the Au concentration should be significantly lower than pure Au concentration at the left boundary and shall not be zero at the right side. This discontinuity of boundary concentration is ignored in the boundary conditions specified in this study due to lack of thermodynamic data to evaluate the exact concentrations, but this simplification does not seem to ruin the effectiveness of the model as evidenced by its successful application to $1\mu\text{m Al} + 1\mu\text{m Au}$ samples..

5.7 Conclusions

A single phase moving boundary model was formulated based on the identification of Au as the main diffusing species in Al-Au system to predict the intermetallic growth. It can

be noted that:

1. This model enables computation of intermetallic growth. However, its effectiveness depends on the accuracy of physical parameters, especially diffusivity.
2. This model assumes Al_2Au_5 as the single phase formed and therefore could only be used to simulate early intermetallic growth when Al_2Au_5 dominates.
3. This model predicts intermetallic growth in $1\mu\text{m Al} + 1\mu\text{m Au}$ system quite accurately, but is not so in $0.3\mu\text{m Al} + 1\mu\text{m Au}$ system because of the incubation required for nucleation in this set of samples.
4. The simplified boundary conditions don't seem to affect the validity of this model despite being thermodynamically inaccurate.

Chapter 6 Oxidation Study of Solid Al-Au Intermetallics

This chapter deals mainly with the oxidation kinetics study of Al-Au intermetallics and the chemical analysis on the oxidized surfaces. AlAu_2 and AlAu_4 , identified in Chapter 4 as the dominant intermetallics after long anneal in two sets of thin films respectively, are selected for the study. Al_2Au is also included in order to outline the trend of Al-Au intermetallics oxidation as Au content increases. For ease of making stoichiometric compounds and characterizing the mass change, solid samples were made instead of thin films.

6.1 Material Identifications

Solid intermetallics, Al_2Au , AlAu_2 and AlAu_4 , synthesized from the pure Al and Au were characterized by differential scanning calorimetry and X-ray diffraction to confirm that the intended phases were indeed obtained. Further, the intention of the characterization is to confirm that the obtained material is single phase, pure intermetallic and that the elements have fully reacted without any residues.

6.1.1 Thermal Identification

For each intermetallic, only one endothermic peak was detected in DSC measurement, indicating that there are no detectable second phases in the synthesized intermetallic. The

DSC diagrams for the three intermetallics are shown in Figs. 6.1-6.3, while the onset temperatures of the endothermic peaks and the expected melting points of the intermetallics extracted from the Al-Au phase diagram in Fig. 2.1 are listed in Table 6.1. The close match of the experimental data to the expected values confirms the intermetallic phases as required.

Fig. 6.1 DSC identification of Al₂Au made by arc melting

Fig. 6.2 DSC identification of AlAu₂ made by arc melting

Fig. 6.3 DSC identification of AlAu₄ made by arc melting

Table 6.1 Transformation temperatures for Al_2Au , AlAu_2 and AlAu_4

	Melting temperatures in phase diagram ($^{\circ}\text{C}$) [Fig. 2.1]	Measured melting temperatures in DSC ($^{\circ}\text{C}$)
Al_2Au	1060	1055
AlAu_2	624	627
AlAu_4	525	526

6.1.2 X-ray Diffraction Identification

Figs. 6.4-6.6 present the XRD patterns obtained for powders of solid Al_2Au , AlAu_2 and AlAu_4 . The standard patterns based on their respective ICSD files are also shown in the figures. The detected XRD peaks appear at the same positions suggested by the standard pattern of every intermetallic and no detectable second phase could be identified.

Fig. 6.4 XRD spectrum of Al_2Au made by arc melting

Fig. 6.5 XRD spectrum of AlAu_2 made by arc melting Fig. 6.6 XRD spectrum of AlAu_4 made by arc melting

6.2 Oxidation Kinetics

The mass gain of solid Al_2Au , AlAu_2 , AlAu_4 and pure Al samples during oxidation at three temperatures were measured by TGA. The conventional data analysis methods such as normalization and linearization were applied to the data at every temperature in order to quantitatively determine the oxidation rate constant and activation energy for all the materials.

6.2.1 Oxidation of Pure Al

Fig. 6.7(a) shows the curves of mass increase ΔW of pure Al specimens during oxidation, which are normalized by the sample area A . At all temperatures, Fig. 6.7(a) presents an initial rapid mass gain and at 1200 min the mass gain is larger as the oxidation temperature increases. According to Equation (2.2)

$$(\Delta W / A)^2 = k_p t ,$$

the square of normalized mass gain $\Delta W / A$ is proportional to the time duration t with a rate constant k_p . Thus plots in Fig. 6.7(a) can be linearized if the square of mass gain is plotted as the Y-axis as in Fig. 6.7(b). After linearization, multi-stage oxidation behavior is observed at each temperature. This is most obvious with the 200°C curve in Fig. 6.7(b) where the initial stage before 200 min is characteristic of non-linear increase of sample mass when the k_p (given by the slope of the curve) varies and thereafter becomes relatively linear with time. The mass gain after 200 min is practically small, which implies that oxidation progresses slowly in this period. At 400°C, the non-linear part becomes barely distinguishable and the parabolic rate law dominates over the majority of oxidation duration so that the 400°C curve becomes a nearly straight line after linearization. The 300°C curve seems to be a transition from 200°C to 400°C. It also

possesses an initial non-linear stage up to 200 min where k_p is varying. Afterwards, the curve approaches to the linear stage. However, unlike the 200°C plot, there is still a slightly noticeable increase in mass after 200 min.

(a) Normalized mass gain versus oxidation time for pure Al

(b) Data from (a) linearized for pure Al

Fig. 6.7 Plots of (a) normalized mass gain versus oxidation time for pure Al and (b) data from (a) linearized for pure Al

6.2.2 Oxidation of Al_2Au

Fig. 6.8(a) shows the normalized mass increase curves of Al_2Au specimens during oxidation. Fig. 6.8(a) is similar to the Al curves of Fig. 6.7(a), except that it shows more mass gain at 300°C. However, at all temperatures Fig. 6.8(b) shows a more linear change up to about 600 min at 200°C and 300°C, and thereafter the curves slightly change the slopes. At 400°C the linear portion appears shorter, around 200-300 min, and the slope changes after that point. The curves each appear to have multiple regions.

(a) Normalized mass gain versus oxidation time for Al_2Au

(b) Data from (a) linearized for Al_2Au

Fig. 6.8 Plots of (a) normalized mass gain versus oxidation time for Al_2Au and (b) data from (a) linearized for Al_2Au

6.2.3 Oxidation of AlAu₂

The normalized mass gain curve at 200°C in Fig. 6.9(a) seems quite similar to that of Al₂Au in Fig. 6.8(a), whereas the 300°C and 400°C curves show steeper increase than those of Al₂Au. After linearization, there is a change of slope at about 100 min in the 200°C curve in Fig. 6.9(b), after which the oxidation rate k_p reduces. The 300°C curve becomes nearly a straight line after linearization, implying that the parabolic rate law dominates at this temperature. The 400°C curve is basically linear too but there seems to exist a slight increase of rate after 500 min.

(a) Normalized mass gain versus oxidation time for AlAu₂

(b) Data from (a) linearized for AlAu₂Fig. 6.9 Plots of (a) normalized mass gain versus oxidation time for AlAu₂ and (b) data from (a) linearized for AlAu₂

6.2.4 Oxidation of AlAu₄

Fig. 6.10(a) shows the normalized mass gain of AlAu₄ at three temperatures. After linearization, the curves in Fig. 6.10(b) show that the initial reaction is non-parabolic at 200°C and 300°C with k_p varying in the region up to 250 min and 350 min for each temperature respectively. At 400°C, the curve appears to be linear up to 400 min after which there is a change in slope. For Al, Al₂Au and AlAu₂, the mass gain increases with temperature, but AlAu₄ apparently gains much more weight on exposure to oxygen at every temperature.

(a) Normalized mass gain versus oxidation time for AlAu₄ (b) Data from (a) linearized for AlAu₄Fig. 6.10 Plots of (a) normalized mass gain versus oxidation time for AlAu₄ and (b) data from (a) linearized for AlAu₄

6.2.5 Oxidation Kinetics of Solid Intermetallics

It is customary to fit the major linear portions of the linearized mass increase curves to determine k_p . The slope of linear fitting for each curve in Figs. 6.7(b)-6.10(b) produces respective k_p at each temperature. Table 6.2 lists k_p values for all samples. This procedure practically means that the phenomena causing the non-linearity are ignored.

The Arrhenius-type Equations (2.3) and (2.4) correlate the oxidation rate constant k_p with the temperature T and the activation energy Q . Plotting $\ln k_p$ against $1/RT$ gives the curves shown in Fig. 6.11. The oxidation activation energies are estimated from the slopes of the curves in Fig. 6.11 and are listed in Table 6.2.

Fig. 6.11 Plots of $\ln k_p$ vs. $1/RT$ from which the activation energy is estimated

Table 6.2 List of oxidation rate constant k_p and activation energy Q values

Material	k_p ($\text{kg}^2 \text{m}^{-4} \text{s}^{-1}$)			Activation energy for oxidation (kJ/mol)
	200°C	300°C	400°C	
Al	6.60×10^{-10}	1.60×10^{-9}	5.80×10^{-9}	27.8
Al_2Au	9.90×10^{-10}	4.50×10^{-9}	8.10×10^{-9}	27.9
AlAu_2	1.49×10^{-9}	5.17×10^{-9}	1.11×10^{-8}	26.7
AlAu_4	2.97×10^{-9}	1.33×10^{-8}	3.93×10^{-8}	33.8

It can be noted that the oxidation rate constant of AlAu_4 is the largest among the materials at every temperature, suggesting that AlAu_4 oxidizes most readily. However, the values obtained herein could not be compared to any literature data as quantitative measurements of the oxidation kinetics of Al-Au intermetallics have not been reported previously. Thus, it is necessary to characterize the oxidation behavior of the intermetallics using other techniques to support the TGA results. In addition, the chemical state change and the oxide layer thickness on the surface after oxidation, which are important to understand the oxidation behaviors, could not be comprehended from TGA measurements. Therefore, surface analysis using XPS was conducted subsequently to investigate over these two points.

6.3 Surface Analysis of Oxidized Solid Intermetallics

XPS shallow surface scan was performed on a series of samples of pure Al and every intermetallic oxidized at 175°C for different times. This is intended to characterize the surface chemical change as a function of exposure time. As the oxide layer could sometimes preclude the photoelectron emission of some element if it is thick enough, and also because it is difficult to determine the oxide thickness from the shallow XPS surface

scan, XPS depth profiling was conducted for the 24 hour oxidized sample of each intermetallic.

6.3.1 XPS Analysis on Pure Al

There exists a wide range of reported values of Al 2p XPS peak positions for Al oxide [109], hence the pure Al samples were heat treated and analyzed using XPS to determine the oxidic and metallic Al 2p peak positions as the reference for subsequent analysis. Fig. 6.12 shows the evolution of the Al 2p spectra as a result of increasing oxidation time, while Fig. 6.13 demonstrates the deconvolution of selected spectra for various oxidation times where the dotted lines are the fitting components corresponding to a particular species and the continuous curves are fitted to the experimental XPS data using these components. The as polished sample shows two clearly distinguishable peaks at binding energy (b.e.) of 75.6 eV and 72.8 eV in Fig. 6.13, which are attributable to the oxidic and metallic Al species respectively according to the values reported by J. A. Taylor [110]. This is in agreement with the common knowledge that Al oxidizes readily and quickly even after a short exposure to air, giving rise to coexistence of two Al species. As time increases, the metallic Al peak at 72.8 eV gradually dwindles while the oxidic peak stands firmly at 75.6 eV. This is indicative of the continuous oxidation of the metallic Al species to form oxide.

Fig. 6.12 Al 2p XPS spectra of pure Al samples oxidized up to 24 hours

Fig. 6.13 Deconvolution of Al 2p XPS spectra of pure Al samples oxidized up to 24 hours

6.3.2 XPS Analysis on Al₂Au

Fig. 6.14(a) displays the evolution of Al 2p spectra for Al₂Au samples oxidized up to 24 hours. Seemingly, there is only one broad peak at all times and it doesn't move with time. This peak, however, can be resolved into two components at b.e. of 75.8 eV and 73.5 eV respectively as shown in Fig. 6.15(a). It can be seen that the 75.8 eV peak is the major contributor to the overall intensity and is attributable to the oxidic Al species referring to the data from pure Al samples. The other one is close to the b.e. of 73.0 eV reported for the Al species in Al₂Au [90–93] and gradually reduces to a weak tail. Apparently, Al₂Au is oxidized even in the as-polished sample, but the oxide is likely to be non-uniform and the oxidation proceeds very slowly with time. Au 4f spectra are shown in Fig. 6.14(b), where two spin-orbit splitted components of the Au peak are clear at all times: the Au 4f_{5/2} branch at 89.1 eV and Au 4f_{7/2} branch at 85.4 eV, close to the values of 89.4 eV and 85.7 eV of Al₂Au reported by J. C. Fuggle *et al* [111]. No change of b.e. seems to happen in the Au 4f spectra with increasing oxidation time and no other peaks can be added into the deconvolution as in Fig. 6.15(b).

(a) Al 2p XPS spectra of Al₂Au samples oxidized up to 24 hours

(b) Au 4f XPS spectra of Al₂Au samples oxidized up to 24 hours

Fig. 6.14 (a) Al 2p and (b) Au 4f XPS spectra of Al₂Au samples oxidized up to 24 hours

(a) Deconvolution of Al 2p XPS spectra of Al_2Au samples oxidized up to 24 hours

(b) Deconvolution of Au 4f XPS spectra of Al_2Au samples oxidized up to 24 hours

Fig. 6.15 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized Al_2Au

Fig. 6.16(a) presents the 3-D montage for the evolution of Al 2p spectra during depth profiling in the 24 h oxidized Al₂Au sample, while Fig. 6.17(a) shows the deconvolution of the experimental peaks. A shoulder at the low b.e. end in Fig. 6.17(a) can be resolved at the non-etched surface indicating that peaks from two species are overlapping. The smaller peak with lower b.e. gradually becomes dominant with increasing depth whilst the peak that was dominant at the surface diminishes. A good deconvolution was obtained with two component peaks at b.e. of 75.8 eV and 73.5 eV as shown in Fig. 6.17(a). The former corresponds well to the Al 2p b.e. in Al₂O₃ while the latter is consistent with reports of Al 2p b.e. in Al₂Au. The evolution of the relative intensities of the component peaks agrees well with the presence of an Al₂O₃ layer on Al₂Au whereby the oxidic peak is dominant at the surface and the Al₂Au peak becomes dominant with increase in depth.

Under these conditions, it is possible to estimate the oxide thickness from the ratio of the area intensities of the oxide and metal peaks using the Strohmeier equation [112]:

$$d \text{ (nm)} = 2.8 \ln \left(1.4 \frac{I_o}{I_m} + 1 \right)$$

where I_o and I_m are the intensities (peak areas) of the oxide and metal photoelectron peaks respectively, which can be readily obtained from the quantification parameters list when deconvoluting the peaks using the CasaXPS software. The successive thicknesses for the oxide layer at each point in the depth profiling are illustrated in Fig. 6.17(a).

The Au 4f spectra obtained in the same sample are shown in Fig. 6.16(b). The deconvolutions in Fig. 6.17(b) demonstrate that two spin-orbit splitted peaks are clear at b.e. of 89.1 eV and 85.4 eV, both within acceptable range of the b.e. values reported by J. C. Fuggle *et al* for Al₂Au. There is no change in the relative peak intensities or b.e. values of Au 4f peaks on depth profiling. This implies that the Al₂O₃ layer does not change the

electronic environment of the Au atoms significantly because the surface and subsurface signals are identical. Therefore, the oxide layer is likely to be thin in this compound allowing Au photoelectrons from the subsurface Al_2Au to reach the detector easily.

(a) Al 2p XPS depth profiling spectra of 24h oxidized Al_2Au (b) Au 4f XPS depth profiling spectra of 24h oxidized Al_2Au Fig. 6.16 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized Al_2Au

(b) Deconvolution of Au 4f XPS depth profiling spectra of 24h oxidized Al_2Au

Fig. 6.17 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized Al_2Au

6.3.3 XPS Analysis on AlAu₂

The Al 2p emissions for AlAu₂ samples oxidized up to 24 hours are shown in Fig. 6.18(a). At all times, the curve shows a single peak with narrower broadness and sharper shape as compared to that of Al₂Au in Fig. 6.14(a). Attempts to deconvolute into component peaks indicated that a single peak at b.e. of 75.8 eV will give a good fit to the data for all oxidizing times as shown in Fig. 6.19(a). Since this b.e. is equivalent to that of oxidic Al, it can be inferred that only Al₂O₃ is detected and that the Al 2p component of AlAu₂ is absent on the surface. This implies a thicker oxide layer on AlAu₂ compared to that on Al₂Au. Au 4f spectra are plotted in Fig. 6.18(b). Two peaks at the b.e. of 88.7 eV and 85.0 eV generate a good deconvolution to the XPS data at all times as shown in Fig. 6.19(b) without any shift in position throughout the duration.

(a) Al 2p XPS spectra of AlAu₂ samples oxidized up to 24 hours

(b) Au 4f XPS spectra of AlAu₂ samples oxidized up to 24 hours

Fig. 6.18 (a) Al 2p and (b) Au 4f XPS spectra of AlAu₂ samples oxidized up to 24 hours

(a) Deconvolution of Al 2p XPS spectra of AlAu₂ samples oxidized up to 24 hours

(b) Deconvolution of Au 4f XPS spectra of AlAu_2 samples oxidized up to 24 hours

Fig. 6.19 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized AlAu_2

Fig. 6.20(a) reflects the evolution of Al 2p spectra of 24 hour oxidized AlAu_2 during depth profiling. The scan on the initial surface generates a single peak, which can be assigned to the oxidic component of Al at 75.8 eV after deconvolution as shown in Fig. 6.21(a). A small tail appears at the low b.e. side after 3 min etching, and evolves into a peak at 73.9 eV in Fig. 6.21(a) after 15 min etching with intensity comparable to the oxidic one. This new peak could be assigned to the emission of Al in AlAu_2 . The oxide peak is generally weakened afterwards but still remains observable till the end of 90 min etching. The evolution of Au 4f spectra is illustrated in Fig. 6.20(b). Deconvolution of the curves as shown in Fig. 6.21(b) manifests a b.e. shift for the two peaks of Au spectra as depth profiling proceeds from the surface to interior: 88.8 eV to 88.2 eV and 85.1 eV to 84.5 eV. H. Piao [15] reported the b.e. of Au 4f peaks in AlAu_2 as 88.6 eV and 84.9 eV, agreeing with the b.e. values obtained on the initial surface of AlAu_2 in our study. However, since the surface is normally oxidized while the interior of the sample should be composed of unoxidized AlAu_2 , 88.2 eV and 84.5 eV are attributed to the Au 4f emissions in AlAu_2 . The b.e. shift with depth profiling signifies that the electronic environment around Au atoms is changed because the oxide layer on AlAu_2 is relatively thick.

(a) Al 2p XPS depth profiling spectra of 24h oxidized AlAu_2 (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu_2 Fig. 6.20 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu_2

(b) Deconvolution of Au 4f XPS depth profiling spectra of 24h oxidized AlAu_2

Fig. 6.21 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized AlAu_2

6.3.4 XPS Analysis on AlAu₄

Al 2p spectra in Fig. 6.22(a) for AlAu₄ samples oxidized up to 24 hours are very similar to those of AlAu₂ in Fig. 6.18(a). Only the oxidic Al component at b.e. of 75.7 eV could be resolved in Fig. 6.23(a), while the Al species in AlAu₄ was masked by it, indicating that the oxide on this compound is thick. The Au 4f spectra are shown in Fig. 6.22(b). In the as-polished state two distinct peaks at b.e. of 87.8 eV and 84.2 eV, corresponding to Au 4f_{5/2} and Au 4f_{7/2} respectively, fit the experimental data very well in Fig. 6.23(b). Since the reported values of b.e. in AlAu₄ are not available for comparison, and further since the Al 2p spectrum clearly indicated a thick oxide layer on these samples, we can not reliably attribute the b.e. values obtained above to the Au 4f doublet in AlAu₄ as a thick oxide layer could preclude the signal from AlAu₄ at layer depths. With increasing oxidation time, it is clear that additional, overlapping peaks become necessary to deconvolute the data. Deconvolution in Fig. 6.23(b) shows that each of the Au 4f doublets could be resolved into two overlapping components; one pair with b.e. of 88.8 and 87.8 eV and another pair at 85.2 and 84.2 eV. Thus, the two additional peaks that appear on increasing oxidation are at the higher energy side of the Au 4f doublet observed in the as-polished sample. There is no evidence for a high b.e. component in the as-polished Al 2p spectra which might indicate differential charging in surface regions. This additional Au 4f doublet appears to represent an Au 4f emission coming from a different chemical environment to that in the as-polished sample [113]. Since the Al 2p shows a thick oxide layer in the 24 hour oxidized sample, the new peaks with b.e. 88.8 and 85.2 eV must be emitted by Au atoms trapped in Al₂O₃.

(a) Al 2p XPS spectra of AlAu₄ samples oxidized up to 24 hours (b) Au 4f XPS spectra of AlAu₄ samples oxidized up to 24 hoursFig. 6.22 (a) Al 2p and (b) Au 4f XPS spectra of AlAu₄ samples oxidized up to 24 hours

(a) Deconvolution of Al 2p XPS spectra of AlAu₄ samples oxidized up to 24 hours

(b) Deconvolution of Au 4f XPS spectra of AlAu₄ samples oxidized up to 24 hours

Fig. 6.23 Deconvolution of (a) Al 2p and (b) Au 4f XPS spectra of oxidized AlAu₄

The evolution of the Al 2p spectra in 24 hour oxidized AlAu_4 sample during depth profiling is shown in Fig. 6.24(a). The non-etched surface scan shows only the oxidic Al 2p peak at a b.e. of 75.7 eV after deconvolution as shown in Fig. 6.25(a). With increasing depth a second peak becomes evident as a shoulder in 15 min, and subsequently as a doublet in 33 min in Fig. 6.25(a). After 15 min ion etching, the oxide layer thickness is reduced to 5.1 nm. Comparison with the Al_2Au ion etching suggests that the initial oxide layer is more than 10.8 nm thick. In 108 mins, the oxidic peak is minor while the second peak is predominant. Deconvolution shows that the second peak should be at a b.e. of 73.7 eV for good fitting to the data. Since this second peak was not detected at the surface, all Al atoms have then been oxidized to Al_2O_3 near the surface. After 108 min etching, the photoelectron signal from the subsurface AlAu_4 is being received and thus the b.e. of Al 2p peak in AlAu_4 can be assigned to 73.7 eV. The Au 4f spectra during depth profiling and the deconvolution to them are shown in Fig. 6.24(b) and Fig. 6.25(b). It is clear that the intensity of the new peaks at 88.8 eV and 85.2 eV rapidly diminish in a short etching time of only 6 min. In the 33 and 108 min etched spectra, deconvolution with peaks at 87.8 and 84.2 eV in combination with very small intensity peaks at 88.8 and 85.2 eV would make no difference to the experimental data. Thus, the peaks with b.e. of 87.8 and 84.2 eV could be attributed to the Au 4f doublet in AlAu_4 while the additional peaks at b.e. of 88.8 and 85.2 eV could be attributed to a new emission from Au atoms trapped in the thick Al_2O_3 layer.

Table 6.3 lists the b.e. of Au 4f and Al 2p XPS peaks measured in both the surface scan and depth profiling for all intermetallics.

(a) Al 2p XPS depth profiling spectra of 24h oxidized AlAu₄ (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu₄Fig. 6.24 (a) Al 2p and (b) Au 4f XPS depth profiling spectra of 24h oxidized AlAu₄

(a) Deconvolution of Al 2p XPS depth profiling spectra of 24h oxidized AlAu₄

(b) Deconvolution of Au 4f XPS depth profiling spectra of 24h oxidized AlAu_4

Fig. 6.25 Deconvolution of (a) Al 2p and (b) Au 4f depth profiling spectra of 24h oxidized AlAu_4

Table 6.3 Summary of binding energy of Al 2p and Au 4f XPS peaks

Materials		Description	
		Al 2p	Au 4f
Al ₂ Au	Surface Scan	Oxide: 75.8eV Al 2p: 73.5eV	Au 4f _{7/2} : 85.4eV Au 4f _{5/2} : 89.1eV
	Depth Profiling	Oxide: 75.8eV Al 2p: 73.5eV	Au 4f _{7/2} : 85.4eV Au 4f _{5/2} : 89.1eV
AlAu ₂	Surface Scan	Oxide: 75.8eV	Au 4f _{7/2} : 85.0eV Au 4f _{5/2} : 88.7eV
	Depth Profiling	Oxide: 75.8eV Al 2p: 73.9eV	Au 4f _{7/2} : 85.1eV→84.5eV Au 4f _{5/2} : 88.8eV→88.2eV
AlAu ₄	Surface Scan	Oxide: 75.7eV	Au 4f _{7/2} : 84.2eV Au 4f _{5/2} : 87.8eV Extra peaks: Au 4f _{7/2} : 85.2eV Au 4f _{5/2} : 88.8eV
	Depth Profiling	Oxide: 75.7eV Al 2p: 73.7eV	Au 4f _{7/2} : 84.2eV Au 4f _{5/2} : 87.8eV Extra peaks: Au 4f _{7/2} : 85.2eV Au 4f _{5/2} : 88.8eV

6.4 Discussion

6.4.1 Multiple Stage Oxidation

The indications from the oxidation kinetics study are that Al-Au intermetallics are indeed able to undergo external oxidation. The TGA results show oxidation reaction persisting for several hundred minutes, which can only be sustained by long-range diffusion of Al from within the bulk of the compound.

At all temperatures, each material appears to undergo multiple oxidation stage, and hence none conforms exactly to a parabolic oxide growth law. At short times of the order of 200

min, the behavior of the Al is non-parabolic at 200°C and 300°C as evident in Fig. 6.7(b). The linear portion at $t > 200$ min of the 200°C and 300°C curves in Fig. 6.7(b) has a reduced slope indicating a slowing down of the oxidation. At 400°C the Al curve appears to undergo parabolic oxidation until around 800 min, at which point there is a change of slope. The intermetallics are also approximately parabolic at 400°C but have inflexions at some point of time. At lower temperatures, the behavior of Al_2Au appears to be parabolic in Fig. 6.8(b) from the start of oxidation at 200°C and 300°C up to 600 min where there is a change of slope. AlAu_2 shows a distinct change of slope in the 200°C curve in Fig. 6.9(b), and a slight change at 500 min in the 300°C curve. AlAu_4 also has a change of slope at about 200 min in the 200°C and 300°C curves in Fig. 6.10(b). Qualitatively similar changes in the low-temperature oxidation behavior have been reported by Lamesle *et al* [114] for doped β -NiAl oxidation. In that report, the initial non-linearity of the oxidation rate constant k_p was attributed to the development of several forms of Al_2O_3 (δ , γ , θ) that grow as Al undergoes bulk diffusion from the interior to the surface of the intermetallic. These forms of Al_2O_3 are believed to be non-uniform and un-protective of the intermetallic surface, thereby allowing further very rapid oxidation and accounting for the k_p variation. Analogously, the inflexions in Figs. 6.7(b)-6.10 (b) may mark the point where the Al_2O_3 structure changes [115,116].

6.4.2 Oxidation Tendency of Al-Au Intermetallics

The values in Table 6.2 show some small increase in k_p of Al_2Au for all temperatures compared to Al but the rates are of the same order of magnitude. However, k_p for AlAu_2 is apparently increased and k_p for AlAu_4 is even consistently an order of magnitude larger than for Al and Al_2Au . This is in agreement with the linearized mass gain curves in Figs. 6.7(b)-6.10(b) that show mass gains in the order $\text{Al} \cong \text{Al}_2\text{Au} < \text{AlAu}_2 < \text{AlAu}_4$. The

activation energy for oxidation is similar for Al, Al₂Au and AlAu₂ but is slightly larger for AlAu₄.

The most striking feature is the consistently more weight gain from Al to AlAu₄ in the order of increasing Au content which, given the decreasing Al concentration, is rather unexpected. For Al₂Au, the Al-richest phase, its close proximity in both k_p and Q values to those of Al suggests Al plays an important role in oxidation. AlAu₂ behaves similarly as Al₂Au at 200°C, but shows a faster mass increase and higher weight gain at 300°C and 400°C. The gold-richest phase, AlAu₄, has a much larger k_p at all temperatures than the other materials, meaning it apparently has a greater tendency to oxidize despite the fact that its Al concentration is the smallest. This is in agreement with XPS depth profiling data, which reflect an increasing oxide layer thickness as Au content increases in intermetallics. A possible explanation for fast AlAu₄ oxidation can be made referring to the melting points of the intermetallics. A high melting point indicates a strong inter-atomic bonding energy, so it has a larger negative free energy of formation. The free energy of formation for Al-Au intermetallics is shown in Table 4.10. AlAu₄ has the lowest free energy of formation among the intermetallics. On the other hand, a low melting point phase has a low binding energy, thus the less stable is the IMC. Consequently, it is easier for Al to break away from Al-Au bond to form Al₂O₃, therefore the faster is the oxidation. Among the intermetallics, Al₂Au has a melting point of 1060°C which is the highest, AlAu₄ has a melting point of about 525°C which is the lowest, and AlAu₂ has a melting point of 624°C which is the middle. The bond energy in AlAu₄ is the weakest, so it will be easiest for Al in it to break away to form Al₂O₃ despite that it has the lowest free energy of formation.

6.4.3 Chemical State Change on Surface After Oxidation

When compared with studies on Al_2Au and AlAu_2 [117–123], AlAu_4 has not been studied adequately. XPS information for this phase is also scarce. The presence of two extra peaks at b.e. of 85.2 eV and 88.8 eV in the Au 4f spectra of AlAu_4 is a new finding in the present work. The formation of known (bulk) oxidized species of Au appears to be unlikely as Au_2O_3 has a Au 4f_{7/2} b.e. near 85.9 eV but is normally formed only under exceptional conditions like exposure of Au to highly reactive ozone [124–127], atomic oxygen [128] or oxygen plasma [129]. Given that AlAu_4 is the gold-richest phase, oxidation of AlAu_4 to Al_2O_3 is more likely to result in the emergence of elemental Au as there is no other known intermetallic that has higher Au than AlAu_4 . The reported b.e. of elemental Au 4f peaks are 87.5 eV and 83.8 eV [130,131]. The peaks observed at 88.8 eV and 85.2 eV in this investigation are significantly higher than the b.e. of elemental Au 4f peaks and thus must be emitted from a different strongly electron-withdrawing chemical environment. As a thick Al oxide is present on the surface, this b.e. shift may result from isolated atoms or nano-colloids of gold surrounded by defect oxygen ions in the oxidized layer.

The b.e. shifts are characteristic of the physical and chemical environment of the analyzed species while the electronegativity determines the type of interaction between the various atoms in the system. The interaction of Au with alumina has been investigated elsewhere [132–137]. J. G. Serrano *et al* found in an XPS study the formation of Al_2Au at the Au-alumina interface at room temperature when Au is sputtered into the alumina matrix, and the elemental Au gets incorporated into Al_2O_3 when Al_2Au disintegrates upon heating resulting in a solid solution of Au in Al_2O_3 where the Au atoms could cluster into nanoparticles [138]. T. P. Nguyen *et al* coated thin gold films on Al_2O_3 ceramic substrate

and reported the initial existence of AlAu_2 as well as subsequent appearance of Al_2Au upon heating at 500°C for 3 hours [139]. Furthermore, T. Atsuko *et al* proved that Au diffused through Al_2O_3 in a Au- Al_2O_3 -Al sandwich to form Al_2Au intermetallic at the Al interface [140]. Thus, dissolution of Au in Al_2O_3 has been suspected in some studies but its characteristic emissions in XPS are not fully understood. This study, while giving a strong indication of dissolution of Au in Al_2O_3 , also measures the Au 4f b.e. of such species. This value will be affected by electronic interaction between Au and the neighboring atoms. In our material system, the b.e. of Au 4f in Al_2O_3 determined is higher than that reported in elemental Au, and that measured here in AlAu_4 . This implies that Au, under these circumstances, has a tendency to donate electrons to the neighboring atoms. Some Au-O bonds may exist to stabilize the Au atoms although no explicit evidence is available for any specific Au oxide species. The Au $4f_{7/2}$ b.e. of 85.2 eV is less than the reported value of 85.9 eV for Au_2O_3 suggesting that any such bonds are not as ionic as the bulk Au_2O_3 oxide.

On the other hand, the solution of Au in Al_2O_3 does not seem to exist on the surface of AlAu_2 . As depth profiling proceeds from surface to the interior of AlAu_2 , there is a small peak shift of 0.5 eV in the Au 4f spectra in Fig. 6.21(b), but no additional peaks are observed. Since the oxide on the AlAu_2 has a moderate thickness as indicated in Fig. 6.21(a), the electronic environment surrounding the Au atoms in AlAu_2 could have been changed but not as much as that in AlAu_4 under the oxidation conditions in present study. Yet, when photoelectrons are emitted from the Au sites, their kinetic energy would be affected by this environmental change, causing a shift of b.e. in the spectra. If either the oxidation temperature or time is increased, there could be additional peaks appearing in the Au 4f spectra when the oxide is thick enough. The oxide on Al_2Au is just too thin to cause any noticeable shift in its Au 4f spectra.

6.4.4 Chemical Reaction in Oxidation

Two processes could take place in oxidation of Al-Au intermetallics: the oxidation of Al element and the phase transformation of intermetallics near the surface due to depletion of Al. As indicated in previous XPS studies on Al-Au thin film alloys [80][90–93], Al_2Au transforms to AlAu_2 during exposure in both open air and moist atmosphere at room temperature. This process could be expressed as follows:

However, this transformation of Al_2Au during oxidation was not observed in the present study. In Fig. 6.15(a), the peak deconvolution proves that Al_2O_3 exists on the surface of solid Al_2Au sample without any sign of AlAu_2 . Then, the oxidation reaction of Al_2Au could be expressed by the following reaction:

where M could be pure Au or any of the Al-Au intermetallics that has a higher content of Au than Al_2Au . The presence of M could not be determined in this study, as no peak shift could be identified for Au up to 24 hour oxidation in Fig. 6.15(b). Fig. 6.17(a) shows the oxide on Al_2Au is very thin (about 10 nm), thus the product M, if formed, might be in minute amount below the apparatus sensitivity and could not be detected. The oxide is obviously thickened on AlAu_2 such that it suppresses the Al 2p emission in this intermetallic in Fig. 6.19(a). When AlAu_2 oxidizes, the following reaction could be expected to take place:

where M could be pure Au, AlAu_4 or Al_2Au_5 . However, the b.e. shift in Au spectra upon depth profiling in Fig. 6.21(b) suggests there is only a change of chemical environment around the atoms due to thickening of oxide, instead of the formation of new species in

which extra peaks would appear. The product M of the oxidation of AlAu_2 could not be determined herein. The oxide thickness on AlAu_4 is the largest among the intermetallics as indicated in Fig. 6.25(a), causing a considerable depletion of Al and the appearance of extra Au peaks in Fig. 6.22(b) attributed to elemental Au trapped in the oxide. Hence, the reaction of AlAu_4 oxidation could be given as:

Therefore, the oxidation of AlAu_4 involves the formations of both oxide and a new species. The oxidation activation energy determined for AlAu_4 in Table 6.2 should account for these two processes, while those for Al_2Au and AlAu_2 mainly represent the oxide formation.

6.5 Conclusions

Solid samples of three selected intermetallics, namely Al_2Au , AlAu_2 and AlAu_4 , were synthesized and their oxidation behavior and its consequences were investigated. Major findings in this study can be summarized as follows:

1. Solid Al-Au intermetallics were successfully synthesized by arc melting the stoichiometric amounts of the elements.
2. Multiple stage oxidation behavior was observed in the weight gain curves for all intermetallics at each temperature. Al and AlAu_4 show non-parabolic growth up to 200 min at 200°C and 300°C, while Al_2Au appears to be parabolic from the beginning of oxidation. The AlAu_2 growth curve at 200°C shows a distinct inflexion but the change of slopes at higher temperatures is small. Parabolic law is generally seen for all intermetallics at 400°C.

3. With the increase of Au content in the intermetallics, the oxidation rate constant k_p is increased in the sequence $\text{Al}_2\text{Au} < \text{AlAu}_2 < \text{AlAu}_4$. The calculated activation energy, Q , is similar for Al, Al_2Au and AlAu_2 , but is slightly higher for AlAu_4 .
4. XPS surface scan shows no peak shift for Al 2p and Au 4f in Al_2Au and AlAu_2 . In AlAu_4 Al 2p is not found to shift but two extra peaks appear at the higher b.e. side in the Au 4f spectra, indicating a substantial reaction has occurred.
5. Deconvolutions of Al 2p XPS surface scan curves demonstrate both the oxide and the Al compound species in Al_2Au , but only the oxidic Al component for AlAu_2 and AlAu_4 . XPS depth profiling reveals the Al 2p compound species in AlAu_2 and AlAu_4 , and the oxide on AlAu_4 is thicker than that on AlAu_2 .
6. The two extra peaks with higher b.e. in the Au 4f XPS spectra of AlAu_4 are attributed to Au species dissolved in Al_2O_3 . The oxide layer on AlAu_2 causes a Au 4f peak shift but is not thick enough to create any new peaks as in AlAu_4 . The oxide on Al_2Au is too thin to cause any change in Au 4f spectra.
7. AlAu_4 has the greatest tendency to be oxidized among the intermetallics tested, suggesting the oxidation of AlAu_4 in wire bond could be a serious reliability problem.

Chapter 7 Relevance to Wire Bonding

It is stated in Chapter 2 that there are some issues that have not been made clear in the study of Al-Au intermetallics, such as the phase formation sequence in isothermal annealing, main diffusant and oxidation of the common intermetallics in air. These problems have been addressed in this project. Although the treatments, characterizations and analysis in this project are not performed on actual wire bond, the findings herein obtained are relevant to the fundamental understanding of wire bonding and the practical reliability assessment. This is discussed in this chapter.

7.1 Interface Transformations Study on Thin Films

The Al-Au thin film samples provide a convenient test vehicle due to its mini size in thickness, allowing for the elemental probing in a direction perpendicular to the interface. The identification of Au as the main diffusant in two sets of samples in this project should also apply to the situation in wire bond since the fundamental mechanisms for intermetallic growth are similar, despite the dimensions being distinctively different. It could also help understand and control the formation of Kirkendall voids frequently encountered in wire bonding due to the uneven fluxes of elements entering and departing a certain location.

The intermetallics formed in wire bonds are generally identified using the Energy Dispersive X-ray (EDX) analyzer attached to SEM. EDX has a limit of spot size, hence could not be reliable if the intermetallic is thin, and neither will EDX give any

information of the microstructure. High resolution TEM are proven in this project to be effective in identifying the intermetallic phases even when they are as thin as 100nm. The unambiguous identification of all intermetallics by TEM consolidates the understanding of the intermetallic formation and transformation in wire bond.

7.2 Modeling for Intermetallic Growth

It is desirable to link the thickness of intermetallics in the wire bond with the strength of wire bond for the sake of reliability control. Conventionally, the thickness of intermetallics is measured from the cross sections of the joint. The single phase moving boundary model developed in this project could provide a computational approach to assess the intermetallic growth in wire bond during processing. Although it could not be directly applied to the long term intermetallic growth when multiple phases coexist, it would be useful, if no incubation is encountered, to estimate the early intermetallic growth when Al_2Au_5 dominates in the joint for a period of time as assumed in the model.

7.3 Oxidation of Common Intermetallics

From an engineering point of view, the present study proves that Al-Au intermetallics, more specifically Al_2Au , AlAu_2 and AlAu_4 , are prone to oxidation when heated in air, among which AlAu_4 oxidizes most readily. This is meaningful when considering reliability of fine pitch wire bonding using ultra thin wires. Since AlAu_4 is frequently the major intermetallic phase in wire bond interfaces due to the excess of Au, package failure due to oxidation of AlAu_4 at elevated temperatures could become a significant problem in microelectronics.

Chapter 8 Summary

The findings of this project cover the Al-Au intermetallics formation, transformation and degradation, all of which are the major factors influencing the reliability of wire bonds. The major conclusions obtained in each chapter are collated here and given as the overall conclusions arising from this project.

8.1 Interface Transformations in Thin Film Diffusion Couples

The following conclusions can be drawn from the investigations conducted in thin film diffusion couples of $0.3\mu\text{m Al} + 1\mu\text{m Au}$ and $1\mu\text{m Al} + 1\mu\text{m Au}$ for interface reactions up to 24-hour isothermal anneals at 125°C , 150°C and 175°C .

1. Al_2Au_5 was the first intermetallic to be detected at the Al-Au interface followed by AlAu_4 in all samples. In $1\mu\text{m Al} + 1\mu\text{m Au}$ samples, however, AlAu_4 was only a transient phase and AlAu_2 formed as the third intermetallic.
2. After prolonged anneal, the predominant intermetallic in $0.3\mu\text{m Al} + 1\mu\text{m Au}$ structure was AlAu_4 , and in $1\mu\text{m Al} + 1\mu\text{m Au}$ was AlAu_2 .
3. The intermetallics were layered with sharp boundaries in accordance with predictions from equilibrium diagram.
4. The O peak observed in the SIMS analysis at the initial Al/Au interface could be used

as an interface marker. Its migration towards the Au layer shows that there is a net Au atom diffusion into Al.

5. The growth kinetics of the intermetallics obey parabolic growth law at 125°C for both structures. At 150°C and 175°C, the parabolic law appears to be obeyed only in the early stages. Subsequently, when either Au or Al is fully consumed, the growth stalls but phase transformations continue towards the intermetallic phase that is thermodynamically most stable under the conditions.
6. The Arrhenius relationships were determined for the parabolic growth rate constants, which show that the activation energy for interface intermetallic growth is 42.298 kJ/mol for 0.3µm Al + 1µm Au structure and 33.602 kJ/mol for 1µm Al + 1µm Au.

8.2 Moving Boundary Model of Intermetallic Growth

A single phase moving boundary model was formulated based on the identification of Au as the main diffusing species in Al-Au system to predict the intermetallic growth. It can be noted that:

1. This model enables computation of intermetallic growth. However, its effectiveness depends on the accuracy of physical parameters, especially diffusivity.
2. This model assumes Al₂Au₅ as the single phase formed and therefore could only be used to simulate early intermetallic growth when Al₂Au₅ dominates.
3. This model predicts intermetallic growth in 1µm Al + 1µm Au system quite

accurately, but is not so in $0.3\mu\text{m Al} + 1\mu\text{m Au}$ system because of the incubation required for nucleation in this set of samples .

4. The simplified boundary conditions don't seem to affect the validity of this model despite being thermodynamically inaccurate.

8.3 Oxidation Study of Solid Al-Au Intermetallics

Solid samples of three selected intermetallics, namely Al_2Au , AlAu_2 and AlAu_4 , were synthesized and their oxidation behavior and its consequences were investigated. Major findings in this study can be summarized as follows:

1. Solid Al-Au intermetallics were successfully synthesized by arc melting the stoichiometric amounts of the elements.
2. Multiple stage oxidation behavior was observed in the weight gain curves for all intermetallics at each temperature. Al and AlAu_4 show non-parabolic growth up to 200 min at 200°C and 300°C , while Al_2Au appears to be parabolic from the beginning of oxidation. The AlAu_2 growth curve at 200°C shows a distinct inflexion but the change of slopes at higher temperatures is small. Parabolic law is generally seen for all intermetallics at 400°C .
3. With the increase of Au content in the intermetallics, the oxidation rate constant k_p is increased in the sequence $\text{Al}_2\text{Au} < \text{AlAu}_2 < \text{AlAu}_4$. The calculated activation energy, Q , is similar for Al, Al_2Au and AlAu_2 , but is slightly higher for AlAu_4 .

4. XPS surface scan shows no peak shift for Al 2p and Au 4f in Al_2Au and AlAu_2 . In AlAu_4 Al 2p is not found to shift but two extra peaks appear at the higher b.e. side in the Au 4f spectra, indicating a substantial reaction has occurred.
5. Deconvolutions of Al 2p XPS surface scan curves demonstrate both the oxide and the Al compound species in Al_2Au , but only the oxidic Al component for AlAu_2 and AlAu_4 . XPS depth profiling reveals the Al 2p compound species in AlAu_2 and AlAu_4 , and the oxide on AlAu_4 is thicker than that on AlAu_2 .
6. The two extra peaks with higher b.e. in the Au 4f XPS spectra of AlAu_4 are attributed to Au species dissolved in Al_2O_3 . The oxide layer on AlAu_2 causes a Au 4f peak shift but is not thick enough to create any new peaks as in AlAu_4 . The oxide on Al_2Au is too thin to cause any change in Au 4f spectra.
7. AlAu_4 has the greatest tendency to be oxidized among the intermetallics tested, suggesting the oxidation of AlAu_4 in wire bond could be a serious reliability problem.

Chapter 9 Recommendations

The properties of Al-Au intermetallics have not been fully understood as of today. This thesis covers results of Al-Au intermetallic growth in thin films and oxidation in solid samples, but these results could be supplemented by work on the following respects:

1. Three intermetallic compositions were selected in oxidation study. As Al_2Au_5 is always the first phase to be formed, it could be added into the scope to generate a complete understanding of the oxidation of Al-Au intermetallics, especially the early stage of oxidation in wire bonds.
2. The structure of oxide layer on the surface of AlAu_4 should be characterized using other high sensitivity surface analysis techniques. TEM observations are only possible if the oxide layer is thick enough.
3. The proposal of oxidation of intermetallics as a failure mechanism in wire bonds needs to be experimentally demonstrated, but this must be conducted with care to eliminate other failure mechanisms that could be operating simultaneously with oxidation to overshadow it.

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