NANOSCALE MICROSTRUCTURAL CHARACTERIZATION OF ALUMINUM AND COPPER BILAYER THIN FILMS DEPOSITED ON SILICON SUBSTRATE USING MAGNETRON SPUTTERING TECHNIQUE

ZULHELMI ALIF BIN ABDUL HALIM

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Mechanical)

Faculty of Mechanical Engineering
Universiti Teknologi Malaysia

SEPTEMBER 2014

To my beloved Mum and Dad.
To all my companions who have accompanied me throughout my life’s journey.
Thanks for everything.

ACKNOWLEDGEMENT

All the praises and thanks be to Allah, the Lord of the ‘Alamin, The Most Gracious, The Most Merciful.

I would like to thank my supervisor, Dr. Muhamad Azizi Mat Yajid, for the patience guidance, encouragement and advice he has provided throughout my time as his student. I feel very fortunate to have a supervisor who cared so much about my work, and who responded to my questions and queries so promptly.

I would also like to thank all the members of staff at Materials Science Lab who helped me during my research. Also, to Mr. Mohamed Mohd Salleh from Ibnu Sina Institute, Mr. Idris from Central Laboratory Universiti Teknologi Petronas and finally Prof Madya. Dr. Nafarizal Nayan from Universiti Tun Hussein for their help and guidance during my experimental works.

And finally to my family, I cannot thank them enough for their encouragement and patience during my study.

ABSTRACT

Aluminum and copper (Al-Cu) bilayer thin films are commonly used as conductors in electronic applications. Unfortunately, the effect of thermal aging on the interfaces of Al-Cu bilayer thin films have led to the formation of intermetallic compounds (IMCs) which eventually degrades the materials. The study of diffusion-reaction in Al-Cu thin film is very challenging compared to the bulk Al-Cu system. From previous related works, the compilation of data regarding the diffusion kinetics in thin film has led to discrepancies due to the complex relationship between the selected experimental parameters and the formation of the IMCs. Therefore, further study is necessary to fully understand the growth kinetics of IMCs particularly for the Al-Cu system. The present work is an attempt to contribute in the understanding of the phase formation by varying the diffusion parameters. Syntheses of the Al-Cu bilayer thin films (800 nm of total thickness) were physically achieved by magnetron sputtering. The bilayer was then aged at temperatures from 100 ^{o}C, 150 ^{o}C and 200 ^{o}C within the duration of one to six hours. The formation of IMCs of different chemical composition and crystallographic structures were characterized by using High Resolution Transmission Electron Microscope (HRTEM), X-ray diffractometer (XRD) and Energy Dispersive X-ray Spectrometer (EDX). Field Emission Scanning Electron Microscope (FESEM) was utilized to study the morphology and the integrity of the bilayer after subjected to aging. Each layer shows both columnar and non-columnar structures which eventually affects the film integrity. The combination of analytical TEM and X-ray diffraction techniques has revealed the formation of several equilibrium phases which could be identified as tetragonal θ-Al_2Cu (*I4mcm*), monoclinic η-AlCu (*I2/m*), orthorhombic ζ-Al_3Cu_4 (*fmm2*) and cubic crystal structure Al_4Cu_9 (*P-43m*). Finally, electrical resistivity test on the bilayer indicates increase in resistivity due to the formation of IMC.

ABSTRAK

Filem nipis dwilapisan aluminum-kuprum (Al-Cu) biasanya digunakan sebagai konduktor dalam aplikasi elektronik. Malangnya, kesan penuaan terma pada bahagian antara muka filem nipis dwilapisan Al-Cu telah membawa kepada pembentukan sebatian antara logam (IMCs) yang akhirnya menurunkan fungsi bahan itu. Kajian tindak balas resapan bagi filem nipis Al-Cu lebih mencabar jika dibandingkan dengan Al-Cu pukal. Daripada penyelidikan sebelumnya, pengumpulan data mengenai kinetik resapan pada filem nipis telah membawa kepada percanggahan kerana hubungan komplek di antara parameter eksperimen terpilih dengan pembentukan IMCs. Oleh itu, kajian selanjutnya adalah perlu untuk memahami sepenuhnya kinetik pertumbuhan IMCs terutamanya untuk sistem Al-Cu. Kajian ini adalah suatu usaha untuk menyumbang kepada pemahaman pembentukan fasa IMCs dengan mengubah beberapa parameter resapan. Sintesis ke atas dwilapisan Al-Cu (berketebalan akhir 800 nm) telah diperolehi secara fizikal dengan kaedah percikan magnetron. Dwilapisan ini kemudiannya melalui proses penuaan pada suhu 100 ^{o}C, 150 ^{o}C dan 200 ^{o}C dalam tempoh antara satu hingga enam jam. Pembentukan IMCs dari komposisi kimia dan struktur kristalografi yang berbeza telah dianalisis mengggunakan Mikroskop Elektron Transmisi Resolusi Tinggi (HRTEM), Pembelauan Sinar-X (XRD) dan Serakkan Tenaga Sinar-X (EDX). Mikroskop Imbasan Elektron (FESEM) telah digunakan untuk mengkaji morfologi dan integriti dwilapisan selepas penuaan. Setiap lapisan menunjukkan struktur turus dan bukan turus yang memberi kesan kepada integriti lapisan. Gabungan analisis TEM dan XRD telah mendedahkan pembentukan beberapa fasa seimbang yang boleh dikenal pasti sebagai tetragonal θ-Al_2Cu (*I4mcm*), monoklinik η-AlCu (*I2/m*), orthorhombic ζ-Al_3Cu_4 (*fmm2*) dan struktur kristal kubik Al_4Cu_9 (*P-43m*). Akhir sekali, ujian kerintangan elektrik pada dwilapisan menunjukkan peningkatan kerintangan kerana pembentukan IMC.

TABLE OF CONTENTS

3 METHODOLOGY

4 RESULTS AND DISCUSSIONS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Y - Sputtering yield

E_T - Maximum energy transferred during sputtering

λ - Mean free path / X-ray wavelength (cm)

K - Binding energy of surface atoms (kJ/mol)

M - Molar weight (kg/mol)

N_a - Avogradro number (1/mol)

jp - Ion current density (A/m^2)

T/T_m - Thornton's model – relative substrate temperature

f.c.c - Face centered cubic

b.c.c - Base centered cubic

W - Intermetallics width (cm)

D - Diffusion rate (cm^2/s)

E_a - Activation energy (kJ/mol)

R - Gas constant (J/molK)

ΔH^o - Change in enthalpy (kJ/mol. at)

C_e - Effective concentration of limiting element

θ (Bragg's) - Bragg's angle

d (Bragg's) - Lattice spacings

$h\ k\ l$ - Crystal plane orientation

a_o - Lattice parameter

$\mathrm{B}_{\mathrm{strain}}$ - Peak broadening contributed by strain (nm)

$\varepsilon_{\mathrm{rms}}$ - Root mean square value of strain (nm)

K_{s} - Scherrer's constant

D_{y} - Crystallites size (nm)

$\mathrm{C}_{\mathrm{hkl}}$ - Dislocation contrast factors

Z - Atomic number

R_{a} - Average surface roughness (nm)

D_{o} - Frequency factor ($\mathrm{m}^2\ \mathrm{s}^{-1}$)

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research background

Since 1970's, the focus of attention on advanced materials and new technologies has been shifted from bulk solid materials towards nano-structured materials like thin films and many research papers related to thin films has been published by researchers from various engineering disciplines. Their research which includes the methods of thin film synthesis, thin film materials system, properties studies and characterization methods has led to the development of impressive technology applications and advanced materials that provide alternative solutions to overcome some deficiency issues in bulk materials.

Al-Cu multilayer thin films are common materials systems which have been studied by several researchers and become an important materials system in microelectronics industries [1-15]. This metal system is used as metallization lines in integrated circuits because of their high conductivity and low material cost if compared to gold (Au). In the recent trend of interconnect design, thin metallization lines have shifted into multilevel metallization (MLM) which allows to the miniaturization of electronic devices.

Silicon and Alumina are the most common semiconductors material used for thin film substrate because they offer good lattice structure for epitaxial growth of most metal films. Besides physical evaporation, molecular beam epitaxy (MBE) and pulse laser deposition technique (PLD), physical sputtering is seen as an effective choice for thin film deposition based on cost and ease of processing, but the quality of the sputtered films is quite uncertain. The thickness of thin films produced by this method can vary from a few nanometers up to micrometer scale in few minutes to a few hours of deposition [16].

However, problem arises when the bimetallic thin films were exposed to heat as it will trigger diffusion between these dissimilar metals. In microelectronic devices, the formation of intermetallics phases within the Al-Cu lines has also meant the degradation of the devices and will eventually lead to device failure. Concern on this issue, had led to effort made by several researchers to the study of diffusion in the Al-Cu binary system [1-15].

The researchers on the binary system have led to discrepancies of results especially on the growth of intermetallics phases. Similar discrepancies were seen on the nucleation kinetics of phases (i.e. diffusion rate and activation energy) and also the formation sequence of the alloying phases. This is due to the complexity of diffusion in thin films which is profoundly differs from diffusion in bulk. Understanding the growth of phase equilibria in bimetallic thin films is crucial for the material design purpose, but it requires a lot of fundamental studies with various experimental parameters.

The present *study* is undertaken *to contribute* to the current understanding of diffusion in Al-Cu thin film system which focus on the bilayers with equal thickness of the individual layers prepared by sputtering deposition. The properties of sputtered thin films and the relations with their substrate are studied using different characterization techniques while the study of diffusion of these bilayers will be focused on low temperature diffusion which is below 300 ^{o}C.

1.2 Problem statement

The discrepancies of data in terms of growth behavior and kinetics are due to the finite volume and also because of the complexity of nanostructure (e.g. structural defects) of the thin films which completely differs from bulk. Previously, different study conditions and analytical methods have been used to understand the behavior. However from our observation, the two most influential parameters are the bilayer thickness ratio and also the range of the aging temperatures. Collective experimental parameters from previous related studies [2-3, 5-7, 12] are illustrated in Figure 1.0. As in this present work, the selected temperatures range is focus on lower temperature which is in between of 100 to 200°C while the total thickness of the bilayers is around 800 to 900 nanometers thick.

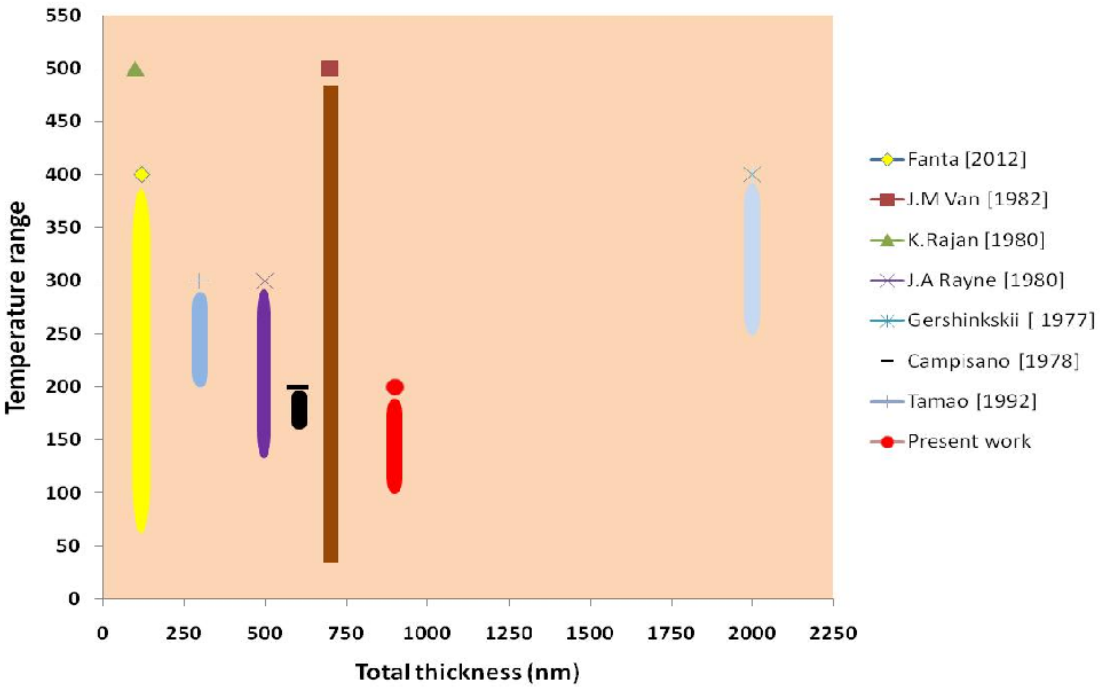

Figure 1.0: Experimental conditions for Al-Cu thin films diffusion study from past authors [2, 3, 5-7, 12].

1.3 Objectives of the research

This research embarks on the following objectives:

1) To establish optimum deposition parameters of thin Al and Cu layers deposition on Si substrate using radio frequency magnetron sputtering deposition.
2) To characterize the properties of bilayers through different thin film characterization techniques including high resolution TEM as a result of different annealing condition.
3) To establish diffusion reaction between the bilayers to promote intermetallics growth through the heat treatment process at different temperatures and time and its effects on structural and electrical properties of the bilayers thin films.

1.4 Research scope

Annealing temperatures, annealing time, initial layer thickness ratio and the crystal structure of the thin films are important parameters which directly influenced the diffusion kinetics and the growth of intermetallics. These parameters were varied by several authors of previous studies [1-15] in order to study and understand the diffusion in thin films. However, this research is concentrated on the polycrystalline Al-Cu thin films where the diffusion mechanism for this particular crystal structure is different from single crystal thin films.

Different from bulk, the geometries of the thin films couple must be considered because of the finite volume for the diffusion process. The formation sequence and the stable end phase of intermetallics in thin films couple is influenced by the layer thickness ratio of the bilayers system. In this research, diffusion of the bilayers with 1:1 thickness ratio is studied.

Diffusion in thin films might occur at relatively low temperatures because of the poor thermal stability in thin films. In this research, the heat treatment of these bilayers was focused on low temperature diffusion within the temperatures range of 100 °C, 150 °C and 200 °C. This temperature range is also simulates the working temperature condition for most electronic devices. Based on the fact that diffusion in thin films is much faster than diffusion in bulk, the annealing time for the bilayers is limited only for a few hours, which is from 1 - 6 hours of the isothermal heat treatment process.

1.5 Research outline

The literature review of this thesis starts with the fundamental knowledge of thin film deposition which focused on the properties of thin films deposited using physical sputtering method. Then, the next sub-chapter in the literature review is concentrated on fundamental knowledge of phase equilibria in binary Al-Cu thin film system. Within this sub-chapter, findings from previous works regarding interdiffusion and intermetallics formation in binary Al-Cu thin films have been discussed. The last sub-chapter in the literature review section has discussed in depth about thin film characterization techniques which have been utilized in this study. The techniques include: the microscopy analysis using FE-SEM and TEM, chemical analysis performed by grazing incident XRD and EDX and lastly the crystal structure analysis of thin film by using electron diffraction pattern and fast Fourier transformation method. Next, in the methodology section, all works in this research which start with the fabrication of the thin films until the characterizations of the thin films are discussed thoroughly. All data from these characterization techniques have been discussed in the section of "Result and Discussion". The growth of intermetallics in the bilayers thin films covers most of the chapter where the chemical properties, crystallographic structure, the kinetics of growth and the effects on the resistivity of the intermetallics phases are discussed in detail. Finally, along with the conclusions, the final chapter describes recommendations for future study on this subject which stressed more on experimental parameters and characterization techniques.

REFERENCES

1. H.Xu, C. Liu, V.V. Silberschmidt (2011). Behavior of aluminum oxide, intermetallics and voids in Cu–Al wire bonds. *Acta Materialia.* (59). pp. 5661–5673
2. F. Haidara, M.C Record, B. Duployer, D. Mangelinck. (2012). Investigation of reactive phase formation in the Al-Cu thin film system. *Surface & Coatings Technology*. 206. pp. 3851-3856
3. J.M Vanderberg and R.A. Hamm. (1982). An In-Situ X-ray studies of phase formation in Cu-Al thin film couples. *Thin solid film*. 97 pp. 313-323.
4. M. Braunovic and N. Alexandrov. (1994). Intermetallic compounds at Al to Cu electrical interfaces: Effect of temperature and electrical current. *IEEE transaction on components, packaging and manufacturing technology*. *A*, 17 (1).
5. K.Rajan, E.R Wallach. (1980). A Transmission Electron Microscopy Study of intermetallic formation in Al-Cu thin film couples. *Journal of Crystal Growth*. (49) pp. 297-302
6. J. A. Rayne, M. P. Shearer and M. L. Bauer. (1980). Investigation of interfacial reactions in thin filmcouples of aluminum and copper by measurement of lowtemperature contact resistance. *Thin solid films,* (65). pp. 381-391
7. A. E. GershinskiiB, I.Fomin, I.Cherepov and L.Edelman (1977). Investigation of diffusion in the Cu-Al thin film system, *Thin Solid Films,*(42). pp. 269-275
8. Y. Guo, G. Liu, H. Jin, Z. Shi, G. Qiao (2011). Intermetallic phase formation in diffusion-bonded Cu/Al laminates. *J Mater Sci*. (46). pp. 2467–2473
9. R. W. Balluffi And J. M. Blakely. (1975). Special Aspects of Diffusion In Thin Films, *Thin Solid Films,* (25). pp. 363-392
10. C.Y Chen and W.S Hwang. (2007). Effect Of Annealing On The Interfacial Structure Of Aluminum Copper Joints. *Materials Transaction*, 7 (48). pp. 1938-1947.
11. Y. Funamizu, K. Watanabe. (1971). *Trans Jpn Inst Met* (12). pp. 147

12. S.U Campisano et.al. (1978). Growth Kinetics Of The θ Phase In A1-Cu Thin Film Bilayers, *Thin Solid Films,* (52). pp. 97-101

13. R. Pretorius, A.M Vredenberg, FW.Saris, R. de Reus. (1991). Prediction of phase formation sequence and phase stability in binary metal-aluminum thin-film systems using the effective heat of formation rule. *J Appl Phys*. (70). pp -3636

14. C.Y Ho, M. W. Aekerman, K. Y. Wu, T. N. Haviii, R. H. Bogaard, R. A. Matula (1983). Electrical Resistivity of Ten Selected Binary Alloy System. *J. Phys. Chem. Ref. Data*. 2(12). pp - 183

15. S. Pfiefer, S. Grossmann, R. Freudenberger, H. Willing, H. Kappl (2012). Characterization of Intermetallic Compounds in Al-Cu-Bimetallic Interfaces. *Electrical Contacts (Holm), IEEE 58th Holm Conference.*

16. Milton Ohring. (1992). *The Material Science of Thin Films*. pp. 109-118. Academic Press INC. London LTD.

17. Donald L Smith. (1992). *Thin films Deposition*. pp. 79-88. McGraw Hill Professional.

18. R.Stuart. (1983). *Vacuum Technology, Thin films, and Sputtering. An introduction*. pp. 123-130. Academic Press INC. London LTD

19. Magnetron sputtering system. Retrieved August 6, 2012 www.d2inlinesolutions.com/technology/sputtering.html

20. SPECS GmbH. Useful Information and Facts about the Practice of Sputtering. Retrieved December 24 2011, from www.specs.de/cms/upload/PDFs/IQE11-35/sputter-info.pdf

21. Charles A. Bishop. (2002). *Vacuum Deposition onto Webs, Films and Foils*. pp 77-78. William Andrew

22. W.K Liu, M.B. Santos. (1999). *Thin films heteroepitaxial systems*. Series on directions in condensed matter physics. Vol.15. pp. 2, 117, 131. World Scientific

23. R. Hvach, D. Novotny and V. Hruby. (2012). *Vacuum*. Vol. 86. pp. 1223-1227.

24. Eugene A. Irene. (2008). *Surface, Interfaces And Thin Films For Microelectronics*. pp. 322. Wiley Interscience.

25. Zhen Guo, Li Tan. (2009). *Fundamentals And Applications Of Nanomaterials*. pp. 23-25. Artech House.
26. W. C. Liu, S. Q. Shi, C. H. Woo and Hanchen Huang. (2002). *Dislocation Nucleation and Propagation During Thin Film Deposition Under Tension*. Computer Modeling in Engineering & Sciences. Vol. 3, No. 2. pp. 213-218
27. I. Petrov. (2003). Microstructural evolution during films growth. *J. Vac. Sci. Techno*. A. 21 (5), pp. s117-s119
28. D.W Pashley. (1975*). Epitaxial Growth. In J.W Matthews* (Ed.) Part B. pp. 1. New York: Academic.
29. John A. Thornton. (1982). *Deposition Technologies for Film and Coatings*. In Rointan F. Bunshah (Ed). pp. 213. Materials Science Series-Noyes Publication
30. CRC Handbook of Chemistry and Physics. (2005). In David R. Lide (Ed). pp. 490-676. 85th Edition. CRC Press.
31. T.B. Massalski. *Binary Alloys Phase Diagrams*. 2nd Edition. American Society for Metals. Ohio: Materials Park. 1990
32. X-ray diffraction. Retrieved January 14 2013. www.nhn.ou.edu/~bumm/Nanolab/ppt/x-ray_diffraction.ppt
33. Mario Birkholz. *Thin Film Analysis by X-ray Scattering*. pp – 113. Weinhem: Wiley-VCH Verlag GmbH & Co. KGaA. 2006
34. C.Suryanarayana, M.G. Norton. X-ray diffraction: *A practical approach*. pp – 99. Springer. 1998
35. J.D Hanawalt. (1986). Manual Search/Match Methods for Powder Diffraction in 1986 .*Powder diffraction journal*. 1(1). pp – 7-13
36. S.Dey, P. Chatterjee, S P Sen Gupta. (2005). J. *Phys. D: Appl. Phys*. 38. pp 1444–1449
37. Brent Fultz James M.Howe. *Transmission Electron Microscopy and Diffractometry of Materials*, 3rd Ed. pp. 61 71 165 200 223. Springer. 2007
38. David B.Williams and C. Barry Carter. *Transmission Electron Microscopy; Basics I*. pp. 7 23 26 69. Springer 1996
39. M.A.Mat Yajid, G.Mobus. (2009). Reactive Multilayers Examined by HRTEM and Plasmon EELS Chemical Mapping. *Microscopy and Microanalysis*. 1 (15). pp 54-61

40. P.J Goodhew, F.J Humpreys: Translated by Zul Azhar Zahid Jamal. "*Mikroskopi Elektron dan Analisis*" 2nd edition. pp 59-66. Penerbit USM 2007
41. Ludwig Reimer. *Transmission Electron Microscopy: Physics of image formation and analysis.* pp – 112-119. Springer-Verlag.1984
42. P.M Budd, P.J Goodhew. *Light Element Analysis in the Transmission Electron Microscope: WEDX and EELS*. Royal Microscopcial Society Microscopy Handbooks 16. pp- 18, 26, 35,38,43. Oxford: Science Publications. 1988.
43. Ivan V. Markov. *Crystal Growth, Fundamentals of Nucleation, Crystal Growth and Epitaxy***.** 2nd edition. pp. 353-450. World Scientific. 2003.
44. H.H Liu, N. Pryds, J. Schou, X. Huang (2010). Quantitative TEM analysis of Al/Cu multilayer system prepared by pulsed laser deposition. *Applied Physics A*. 101. pp. 677-680
45. H.Niwa and Masaharo Kato (1992). Single Crystal Al Grown by Sputtering on (111) Si Substrate. *Appl. Phys. Lett.* (60.) 20. pp. 2520-2521.
46. Y. Choi, S. Suresh. (2002). Size effects on the mechanical properties of thin polycrystalline metal films on substrates. Acta Materialia (50) pp. 1881–1893
47. A. M. Chaplanov,M. I. Markevich. (2003). Recrystallization Behavior of Thin Metal Films during Isothermal and Pulsed Annealing. (39), 3, pp. 257-259
48. B. Bhushan. *Handbook of Nanotechnology*. pp. 1035. Springer 2nd edition. 2007
49. T. Ungar. (1997). Strain broadening causes by dislocation. JCPDS-International Centre for Diffraction Data.
50. Grazing incident angle thin film analysis. www.handmanalytical.com/pdfs/grazing_incidence.pdf. Retrieved April 6, 2012
51. L.D. Gulay, B. Harbrecht. (2004). The crystal structure ofζ-Al_3Cu_4. *Journal of Alloys and Compounds* (367). pp 103–108

52. X.L. Ma, A. Rudiger, H. Liebertz and U. Koster. (1998). A new structural variant of ζ-Al_3Cu_4 and its orientation relationship with the cubic γAl_4Cu_9. *Scripta Materialia*, (39), No. 6, pp. 707–714
53. Y. Kajikawa, S. Noda, H. Komiyama. (2002). Preferred Orientation of Chemical Vapor Deposited Polycrystalline Silicon Carbide Films. *Chemical Vapor Deposition*. (8). 3. pp. 99–104
54. K. Gao, S.M. Li, H.Z. Fu. (2011). Intermetallic Al_2Cu orientation and deviation angle measured by the rotating directional test during directional solidification. *Adv. Mat. Lett.* 2(5) pp. 368-372.
55. Y. Tamou, J. Li, S. W. Russell and J.W. Mayer. (1992). Thermal and ion beam induced thin film reactions in Cu-Al bilayers. *Nuclear instruments and Methods in Physics Research B.* (64) pp. 130-133
56. H.J Klaar and F.Y. Hsu. (1996). New Preparation Method for Cross-Sectional TEM Specimens. *Materials Characterization*. 36(4) pp. 365-369.
57. D.L Beke, A.Lakatos, G. Erdelyi, A. Makovecz, G. A. Langer, L.Daroczi, K. Vad, A.Csik. (2011). Investigation of grain boundary diffusion in thin films by SNMS technique. *Diffusion in Solids and Liquids VI.* Vol. 312-315 pp 1208-1215
58. M.T Le, Y.U Sohn, J.W Lim, and G.S Choi. (2010). Effect of Sputtering Power on the Nucleation and Growth of Cu Films Deposited by Magnetron Sputtering. *Materials Transactions*. Vol. 51. pp 116-120.
59. H. Chen, Y. Lu, and W. Hwang. (2005). Effect of Film Thickness on Structural and Electrical Properties of Sputter-Deposited Nickel Oxide Films. *Materials Transaction*. Vol 46(4). pp. 872-879.
60. S. Terada, H. Murakami, K. Nishihagi. (2001). Thickness and Density Measurement for New Materials with combined X-ray Technique. *IEEVSEMI Advanced Semiconductor Manufacturing Conference*. pp. 125-129
61. H.T.G. Hentzell, R.D. Thompson and K.N. Tu. (1983). Motion of W marker dual sequential compound formation in bimetallic Al-Cu thin films. *Materials letter.* Vol 2 (2). pp. 81-84
62. T.C Wei and R.Daud (2002). The effects of aged Cu-Al intermetallics to electrical resistance in microelectronics packaging. *Microelectronics International*. Vol 19 (2). pp. 38-43