

"Investigation of solid state reactions in Copper-Tin thin film systems"

A Thesis

submitted in partial fulfillment of the requirements for M.Sc. Degree in physics

By

Hanaa Zaka Felfel Gendi

B.Sc. Degree in physics

2012

Supervisors

Prof.Dr. / Mohamed Medhat Abd El Rahman Hafez

Prof.Dr. / Suzan Mohamed Salah El-Dien Fouad

Prof.Dr. / Dezso Laszlo Beke

To

Department of physics Faculty of Science Ain Shams University 2016

Abassia- Cairo- Egypt- Tel. (202) 26857 769- Fax: 0020224662917-Postal code 11566.

Site: http://Sci.Shams.edu.eg



" دراسة التفاعلات في الحالة الصلبة لنظم أغشية رقيقة من نحاس- قصدير"

رسالة مقدمة للحصول على درجة الماجستير في العلوم كجزء مكمل لمتطلبات رسالة الماجستير بكلية العلوم

"الفيزياء"

من هناء زكا فلفل جندي بكالوريوس العلوم في الفيزياء ٢٠١٢

لجنة الإشراف

أ ١٠/ محمد مدحت عبد الرحمن حافظ

أستاذ فيزياء البصريات – كلية العلوم – جامعة عين شمس أ ٠ د/ سوزان محمد صلاح الدين فؤاد

أستاذ فيزياء الجوامد – كلية التربية – جامعة عين شمس أ • د/ دجا لاسلو باكا

أستاذ فيزياء الجوامد - كلية العلوم و التكنولوجيا - جامعة ديبرزين بالمجر المحر المحر المحر المحر المحر المحر المحرد المحرد

قسم الفيزياء كلية العلوم- جامعة عين شمس

7.17

العنوان: العباسية – القاهرة – جمهورية مصر العربية. تليفون/769 26857 (202). فاكس/002022466291. الرقم البريدي/11566.

Site: http://Sci.Shams.edu.eg

"Investigation of solid state reactions in Copper- Tin thin film systems"

By

Hanaa Zaka Felfel Gendi

Supervisors

Signature

Prof.Dr. / M. Medhat

Prof. of optics Faculty of Science Ain Shams University

Prof.Dr. / S. S. Fouad

Prof. of solid state Faculty of Education Ain Shams University

Prof.Dr. / D. L. Beke

Prof. of solid state Faculty of Science and Technology Debrecen University



MEMORANDUM OF AGREEMENT BETWEEN

AIN SHAMS UNIVERSITY (CAIRO-EGYPT)

and



UNIVERSITY OF DEBRECEN FACULTY OF SCIENCE AND TECNOLOGY (DEBRECEN, HUNGARY)

WHEREAS

The representatives of AIN SHAMS UNIVERSITY, CAIRO, EGYPT (ASU) and UNIVERSITY OF DEBRECEN FACULTY OF SCIENCE AND TECHNOLOGY (UD FST), DEBRECEN, HUNGARY

- 1. Are convinced that cooperation is essential in order to strengthen the relationship between people.
- 2. Share interests in similar academic, scientific and professional goals.
- 3. Intend to increase the human and professional relations, which contribute to achieving the aims, which both pursue.

It is therefore agreed:

ARTICLE I

To promote the development of academic, scientific, technical and cultural relations between ASU and UD FST, through not restricted to academic exchanges, scientific research, professional internships and technical cooperation.

ARTICLE II

The two partners agree on achieving cooperation through:

- 1. Exchange of professors, researchers and students.
- Exchange of information, curricula, references, research papers and publications.
 Information shared in this way are to be used exclusively by the parties to enhance their cooperation and must not be disclosed to third parties.
- Collaboration in joint research projects and joint supervision of MSc and PhD degrees and professional diplomas.

ARTICLE III

- The authority of each party will do its best to secure funds to cover expenses of cooperative activities.
- Such expenses will be agreed upon by both parties before the start of each activity.
- Details about specific actions are to be detailed and signed in a separate agreement based on the present memorandum.

ARTICLE IV

Each party will appoint a coordinator who will be responsible for developing an annual plan for the activation of the agreement.

ARTICLE V

The term of duration will be for two years to be automatically renewed for equal periods unless one of the parties notified in writing to the other of its intent to terminate the agreement at least six months prior the renewal date.

ARTICLE VI

This agreement will become effective immediately upon signing by both parties after the approval of concerned authorities.

ARTICLE VII

In the event of a dispute between the parties arising out or relating this agreement, regarding its interpretation or execution or any other related matter, shall be settled amicably by alternative methods of dispute resolution.

On behalf of

Ain Shams University:

Prof. Dr. Aly Al-Gamal

Dean

Prof. Dr. Suzan Fouad Coordinator

Department of Physics

Prof. Dr. Hussein Essa

President

On behalf of the

White Sign of Debrecen, Faculty of Science

Prof. Dr. Akos Pintér

tololi

Prof. Dr. Dezső Beke

Department of Solid State Physics

13072

Acknowledgement

My very deep gratitude goes to Prof.Dr. Salah Yaseen El-Bakry, chairman of the physics department at Faculty of Science-Ain Shams University and also Prof.Dr. Mahmoud Yaseen El-Bakry, chairman of the physics department at Faculty of Education-Ain Shams University for their interest, fruitful comments, support and encouragement.

I would like to thank my advisor Prof.Dr. Suzan Mohamed Salah El-Dien Fouad for her excellent supervision and guidance throughout the duration of my work and for making the agreement between Faculty of Education, Ain Shams University, Egypt and Faculty of Science and Technology, Debrecen University, Hungary.

I also wish to thank Prof.Dr. Mohamed Medhat Abd El Rahman for his support and understanding. Special thanks for giving me helpful comments.

Thanks so much to Prof.Dr. Dezso Laszlo Beke for giving me the opportunity to be introduced to the solid state diffusion world. His patience, guidance and great help to make this work possible.

I am also thankful to Dr. Shenouda Shanda Shenouda for his help and contribution regarding to the experimental work.

This thesis is dedicated to my parents and also the rest of my family.

This project was funded by the (OTKA) Grant No. NF 101329 as well as by the European Union and the state of Hungary, co-financed by the European Social Fund in the framework of the TÁMOP 4.2.4. A/2-11-1-2012-0001 'National Excellence Program (author G.L. Katona) and TÁMOP- 4.2.2.A-11/1/KOV-2012-0036 projects.

Abstract

Abstract

The problem of solid-state reactions in nanostructured thin film system with individual thicknesses of few nanometers is still a challenging subject. If the films are nanocrystalline, the mass transport along different grain boundaries (GBs) can have an important effect on the entire intermixing process.

Solid state reactions between nanocrystalline Cu and Sn films are investigated at room temperature by depth profiling with secondary neutral mass spectrometry and by X-ray diffraction. A rapid diffusion intermixing is observed leading to the formation of homogeneous Cu₆Sn₅ layer. There is no indication of the appearance of Cu₃Sn phase. This offers a way for solid phase soldering at room temperature, i.e. to produce homogeneous Cu₆Sn₅ intermetallic layer of several tens of nanometers during reasonable time (in the order of hours or less). The growth kinetics and phase formation mechanism of Cu₆Sn₅ are studied. From the detailed analysis of the growth of the planar reaction layer, formed at the initial interface, the value of the parabolic growth rate coefficient at room temperature is estimated. In addition, the overall increase of the composition near to the substrate inside the Cu film is interpreted by grain boundary diffusion induced solid state reaction: the new phase is formed along the grain boundaries and grows perpendicular to the boundary planes. From the initial slope of the composition versus time function, the interface velocity during this reaction is estimated.

Abstract

Copper- tin (Cu-Sn) layers are of great technological and scientific interest, and are frequently used to avoid health and environmental problems caused by the use of lead- based alloys. Sn thin films deposited on Cu- based substrate are often used for soldering of nanoelectronics devices.

Keywords: Cu-Sn nanostructured thin films; growth kinetic studies; SNMS depth profiling; solid state reactions; soldering.

List of figures

	Page
Figure 1.1: The distribution of atoms inside the materials a) before diffusion b) after diffusion.	10
Figure 1.2: The concentration profiles for the materials a) before diffusion b) after diffusion.	11
Figure 1.3: Vacancy mechanism.	12
Figure 1.4: The diffusion positions in the polycrystalline material.	13
Figure 1.5: Schematic illustration of the order of magnitude of different coefficients D on the inverse temperature relative to T_m/T (Arrhenius diagram).	13
Figure 1.6: Diffusion process in solids in one dimension.	14
Figure 1.7: Schematic diagram shows the formation of intermetallic phase.	16
Figure (1.8 a, b): (a) Atomic currents J _A and J _B and (b) the result of interdiffusion schematically in an AB diffusion couple.	20
Figure 1.9: Fisher's model of GB diffusion.	24
Figure 1.10: Schematic illustration of Harrison's diffusion regimes.	24
Figure 1.11: Schematic diagram of DIGM in a region of a grain boundary. (a) Solute atoms are deposited during grain boundary diffusion,	26

and the boundary migrates while leaving behind an alloyed zone. (b) Solute atoms are removed during grain boundary diffusion, and the boundary migrates while leaving behind a de- alloyed zone.	
Figure 1.12: Diffusion and formation of reaction layers around GBs in an A/B thin film, schematically. A and B are blue (dark grey) and green (light grey) and the reaction layers are in light blue (lighter grey) and brown (darker grey), respectively.	27
Figure 1.13: Concentration-depth profile shows the DIGM process.	28
Figure 1.14: TEM for Fe-Zn to show the effect of DIR and DIMG [55].	30
Figure 1.15: Schematic illustration of a Cu-Ni diffusion couple with zones of different microstructure [56].	31
Figure 1.16: Phase diagram of Cu-Sn.	33
rigure 1:10. I have diagram of Ca on.	33
Figure 2.1: Sputtering process.	35
Figure 2.1: Sputtering process. Figure 2.2: Schematic diagram of typical magnetron	35
Figure 2.1: Sputtering process. Figure 2.2: Schematic diagram of typical magnetron sputtering system. Figure 2.3: DC magnetron sputtering machine used in	35 36
Figure 2.1: Sputtering process. Figure 2.2: Schematic diagram of typical magnetron sputtering system. Figure 2.3: DC magnetron sputtering machine used in Debrecen. Figure 2.4: Schematic diagram of secondary neutral	35 36 37

Figure 2.7: Sprofilometer w	Schematic diagram shows how sty orks.	ylus 43
Figure 2.8 : Sc	chematic diagram of XRD process.	45
O	stack shows different substrates that ffusion barrier.	t do 46
	Comparison between SiN, SiCN, MS technique [83].	and 47
O	A stack shows that the SiN is a er unlike other different substrates.	Cu 48
	a) Intensity versus sputtering time versus depth of the as-deposited Srn).	
O	Concentration versus depth of the (25 nm)/SiN for 0.5 h.	aged 52
O	Concentration versus depth of the (25 nm)/SiN for 1 h.	aged 52
O	Concentration versus depth of the (25 nm)/SiN for 2 h.	aged 53
	Concentration versus depth of the (25 nm)/SiN for 4 h.	aged 53
C	Concentration versus depth of the (25 nm)/SiN for 6 h.	aged 53
S	Concentration versus depth of the (25 nm)/SiN for 20 h.	aged 53
	Concentration versus depth of the (25 nm)/SiN for 26 h.	aged 54
Figure 3.9: (Concentration versus depth of the	aged 54

Sn(50 nm)/Cu(25 nm)/SiN for 75 h.	
Figure 3.10: Concentration versus depth of the aged Sn(50 nm)/Cu(25 nm)/SiN for 168 h.	54
Figure 3.11: Concentration versus depth of the aged Sn(50 nm)/Cu(25 nm)/SiN for 528 h.	54
Figure 3.12: Concentration versus depth of the aged Sn(50 nm)/Cu(25 nm)/SiN for 3 months.	55
Figure 3.13: Concentration versus depth of the aged Sn(50 nm)/Cu(25 nm)/SiN for 1 year.	55
Figure 3.14 : X-ray diffraction for Sn (100 nm)/Cu (50 nm)/SiN (a) as-deposited, (b) aged for 2 h, and (c) aged for 533 h. The dashed lines show the expected positions of Cu ₃ Sn: no Cu ₃ Sn was detected.	57
Figure 3.15: (a) Intensity versus sputtering time, (b) Concentration versus depth of the as-deposited Sn (100 nm)/Cu (50 nm)/SiN.	58
Figure 3.16: Concentration versus depth of the aged Sn(100nm)/Cu(50nm)/SiN for1 h.	59
Figure 3.17: Concentration versus depth of the aged Sn(100nm)/Cu(50nm)/SiN for 2 h.	59
Figure 3.18: Concentration versus depth of the aged Sn(100nm)/Cu(50nm)/SiN for 4 h.	59
Figure 3.19: Concentration versus depth of the aged Sn(100nm)/Cu(50nm)/SiN for 6 h.	59
Figure 3.20: Concentration versus depth of the aged Sn(100nm)/Cu(50nm)/SiN for 8 h.	60
Figure 3.21: Concentration versus depth of the aged	60

Figure 3.33: Concentration versus depth of the aged	66
Sn(200nm)/Cu(100nm)/SiN for 3.5 h.	
Figure 3.34: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 7 h.	66
Figure 3.35: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 25 h.	67
Figure 3.36: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 50 h.	67
Figure 3.37: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 7 d.	67
Figure 3.38: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 16 d.	67
Figure 3.39: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 25 d.	68
Figure 3.40: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 45 d.	68
Figure 3.41: Concentration versus depth of the aged Sn(200nm)/Cu(100nm)/SiN for 250 d.	68
Figure 4.1: XRD patterns for Cu/Sn couple with 1 µm-thick Sn layer aged for various times at room temperature (a) 0 d; (b) 5 d; (c) 10 d; (d) 20d; (e) 40 d; and (f) 76 d (Ref [32]).	70
Figure 4.2: XRD patterns for Cu/Sn couple with 1µm-thick Sn layer aged for various times (a) 373 K, 1 h; (b) 398 K, 1 h; (c) 423 K, 0.5 h; (d) 473 K, 0.5 h (Ref [32]).	71
Figure 4.3: SEM of the as-deposited Sn (100 nm)/Cu	73