



**PREPARATION AND CHARACTERIZATION OF BULK
NANOPOROUS Sn, SnO₂ AND Zn**

by

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A thesis submitted in fulfillment of the requirements for the degree of
Master of Science (Microelectronic)

**SCHOOL OF MICROELECTRONIC
UNIVERSITI MALAYSIA PERLIS**

2013

ACKNOWLEDGEMENTS

In the name of Allah, the most gracious and the most merciful. Alhamdulillah, all praises to Allah for the strengths and His blessing in completing this thesis. Special appreciation goes to my supervisor, Dr. Mohamad Halim Abd. Wahid, for his supervision and constant support. His invaluable help of constructive comments and suggestion throughout the experimental and thesis works have contributed to the success of this research. Not forgotten, my appreciation to my co-supervisor, Mr. Shamsul Amir Abdul Rais for his support and knowledge regarding this topic. I would like to express my appreciation to the former Dean School of Microelectronic Engineering, Associate Prof. Dr. Johari Adnan and new Dean School of Microelectronic Engineering, Dr. Rizalafande Che Ismail for their support and help towards my postgraduate affairs.

My acknowledgement also goes to all lecturers and staffs at School of Microelectronic Engineering, UniMAP for their kindness and co-operations. Thanks to all laboratory technicians especially Mr. Bahari Man for their technical assistance during this work. I would like to extend my heartiest appreciation to Ministry of Higher Education (MOHE) for providing me with mymaster scholarship to assist my studies financially as well as the allocation for funding this research through FRGS grant 9003-00269 and 9003-00312. Sincere thanks to all my beloved friends especially Meor, Najib, Amin, Anas and others for their kindness and moral support during my study. Thanks for the friendship and memories.

Last but not least, my deepest gratitude goes to my adored parents, Mr. Ahmad Shahar Saaludin, Mrs. Salihah Salleh and also to my brothers and sister for their endless love, prayers and encouragement. Also not forgetting my beloved fiance, Rozitah Isnin for his invocation, warmness love, support and encouragement throughout this study. To those who indirectly contributed in this research, your kindness means a lot to me.

Thank you very much.

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LIST OF SYMBOLS, ABBREVIATIONS OR NOMENCLATURE

EUVL	Extreme Ultraviolet Lithography
XUV	Soft X-ray
Sn	Tin
SnO ₂	Tin Oxide
Zn	Zinc
pL	Photoluminescence
Si	Silicon
SiO ₂	Silicon Oxide
LPP	Laser Produce Plasma
DPP	Discharge Produce Plasma
ILE	Institute Of Laser Engineering
MEXT	Ministry Of Education, Science and Technology
CO ₂	Carbon Dioxide
DNA	Deoxyribonucleic Acid
NaOH	Sodium Hydroxide
DI	Deionised
SEM	Scanning Electron Microscope
AFM	Atomic Force Microscope
TEM	Transmission Electron Microscope
SIMS	Secondary Ion Mass Spectrometry
Al	Aluminum
HF	Hydrofluoric Acid
FESEM	Field Emission Scanning Electron Microscope
ICs	Integrated Circuits

LLNL	Lawrence Livermore National Laboratories
SNL	Sandia National Laboratories
EUV LLC	Extreme Ultraviolet Limited Liability Company
MBDC	Mask Blank Development Center
RTC	Resist Test Center
EUCLIDES	Extreme UV Concept Lithography Development System
ASET	Super-Advanced Electronics Technologies
REB	Relativistic Electron Beams
MEMS	Micro-Electro-Mechanical-Systems
KrF	Krypton Fluoride
ArF	Argon Fluoride
XeCl	Xenon Chloride
EBL	Electron-Beam lithography
LD	Laser Diode
SLS	Selective Laser Sintering
BETS	Bis Ethylenedithio Tetraselenafulvalene
LASER	Light Amplification by Stimulated Emission of Radiation
PVA	Polyvinyl Alcohol
PEG	Polyethylene Glycol
MSDS	Material Safety Data Sheets

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ABSTRAK

Litografi ultraungu melampau (EUVL) menerima banyak perhatian kerana potensinya dalam pembuatan jumlah yang tinggi (HVM) untuk litar bersepadu (IC). Kajian ini menyumbang kepada kajian sasaran sumber ultraungu melampau (EUV). Dalam dunia pelan hala tuju masa depan semikonduktor menyatakan keperluan bagi nod bersaiz kecil pada wafer (Sejenis silikon). Adalah penting untuk sasaran sumber menghasilkan panjang gelombang pendek 13.5 nm yang mempunyai pemantulan tertinggi bagi berbilang salut Mo / Si cermin iaitu kira-kira 70 %. Kaedah laser yang dihasilkan plasma (LPP), didorong oleh 1.06 μm neodimium- doped yttrium aluminium garnet (Nd:YAG), karbon dioksida (CO_2) laser sesuai untuk mencapai sasaran sumber gelombang pendek. Penyelidik di seluruh dunia secara intensif mencari sumber yang paling sesuai untuk calon target. EUV laser sistem semasa ini menggunakan titisan cecair timah sebagai sumber mempunyai kelemahan menjana serpihan. Tujuan projek ini adalah untuk menghasilkan sasaran sumber yang bersifat berliang dan berkepadatan rendah. Mewujudkan struktur berliang nano sebahagian besar adalah salah satu penyelesaian untuk mencapai sasaran berketumpatan rendah yang akan membuatkan sasaran ideal berketumpatan rendah plasma target. Sn, SnO_2 dan Zn dipilih kerana potensi mereka sebagai EUV dan XUV (X-ray lembut) yang mana sasaran sumber mempunyai kemampuan penukaran yang tinggi. Kaedah serbuk metalurgi telah dipilih dan digunakan dalam fabrikasi sampel yang mana konsep ini telah dikenali dengan secukupnya untuk menghasilkan sampel yang sangat berliang. Parameter yang terlibat dalam penyediaan sampel pukal berliang nano seperti masa, diameter, suhu, nisbah, tekanan, pemilihan pengikat dan lain-lain adalah penting dan perlu penilaian berhati-hati atas aplikasinya. Projek penyelidikan ini dibahagikan kepada dua bahagian utama iaitu persediaan dan pencirian. Parameter yang digunakan dalam proses penyediaan ini dijangka menjadi penanda aras untuk rujukan dalam penyelidikan yang berkaitan pada masa depan. Mikroskop berkuasa tinggi iaitu SEM telah digunakan untuk menganalisis pencirian struktur berliang. Selain itu, XRD telah dilakukan dalam mengkaji fasa sampel bersama-sama dengan bahan-bahan yang tidak diketahui. Bagi menganalisis sampel galangan, galangan spektroskopi elektrik telah digunakan. Perubahan parameter yang dipilih dalam proses persediaan telah mempengaruhi hasil daripada analisis yang sewajarnya. Dalam keadaan tertentu, struktur berliang memaparkan laluan pengalir yang rendah yang menunjukkan beberapa ketidakserasian dalam kekonduksian elektrik. Projek ini telah menghasilkan keputusan yang baik dalam menyediakan struktur berliang pukal yang mana liang nano telah dicapai. Daripada penyelidikan ini menunjukkan potensi struktur berliang berketumpatan rendah dikenal pasti untuk menjana idea-idea dalam mengatasi masalah serpihan untuk kebaikan aplikasi peranti pada masa depan.

ABSTRACT

Extreme ultraviolet lithography (EUVL) has garnered much attention due to its potential in high-volume manufacturing (HVM) of integrated circuit (IC). This research contributes to the study of EUV source target. It has been stated that in the world of semiconductor future roadmaps, there is a need for the small-sized node on the wafer. It is essential for the source target to produce a short wavelength of 13.5 nm, which has the highest reflectivity for multicoated Mo/Si mirror, around 70%. The laser-produced plasma (LPP) method, driven by 1.06 μm neodymium-doped yttrium aluminium garnet (Nd:YAG), carbon dioxide (CO_2) laser is suited to achieve short wavelength target sources. Researchers around the world have been intensively searching for the most suitable source target candidate. The current EUV laser system employs liquid tin droplet, which has a weakness of generating debris. This project proposes to produce a source target of a porous nature and of low density. Creating the bulk nanoporous structure is one of the solutions to achieve a low density target, which would make an ideal low-density plasma target. Sn, SnO_2 and Zn are chosen due to their potential as EUV and XUV (soft X-ray) source targets that are capable of high conversion. The method of powder metallurgy has been selected and applied in sample fabrication, where this concept has been known to adequately produce highly porous samples. Parameters involved in the bulk nanoporous sample preparation, such as time, diameter, temperature, ratio, pressure, binder selection and others, are crucial and need careful evaluation upon application. This research project is divided into two main parts, namely preparation and characterization. The parameters applied in the preparation process are expected to become the benchmark for reference in future related researches. The high-powered microscope, namely SEM, was used to analyse the characterization of porous structure. Besides that, XRD was performed in studying the phase of the samples along with unknown substances. As for analysing sample impedance, electrical impedance spectroscopy was employed. The selected parameter variation in the preparation process had influenced the result of analysis accordingly. In certain situations, the porous structure displayed a low conductive path, showing some incompatibility in electrical conductivity. The project has produced favourable results in preparing the bulk porous structure, where nanopores have been achieved. From the research, the potential of low-density porous structure has been identified to generate some ideas in overcoming the debris problem for the betterment of future device applications.

CHAPTER 1

INTRODUCTION

1.1 Historical Background.

Extreme Ultraviolet Lithography (EUVL) is likely the future equipment for the large volume production of integrated circuit having a node sized less than 40 nm. Although fabrication techniques such as ion beam bombardment are available for small sized node on the wafer, they are not economical for mass production. With EUVL, the fabrication rate of wafer can reach up to 100 wafers per second.

The 13.5 nm wavelength has been chosen as it has the highest reflectivity for multicoated Mo/Si mirror, which is around 70%. Producing such a laser source is made possible by using Laser-Produced Plasma (LPP), with a laser at a wavelength of 1.06 μm (Nd:YAG, CO₂ laser) being used as a driver laser. As for the plasma, Xe and Sn targets are used as the target materials for laser irradiation. Plasma produced Sn LPP shows conversion efficiency of several times higher than those by Xe targets. Higher conversion rates of 13.5 nm light can be achieved by maintaining low electron density in the produced plasma [1].

To control electron density, low density Sn targets are used as the target in the lithography process. At the Institute of Laser Engineering (ILE), Osaka University, low density Sn foam targets used with Nd:YAG laser shows conversion efficiency of 3% at 2% bandwidth [2]. However, another lithography system that uses liquid Sn target and

CO₂ laser proved to have better conversion rate, thus taking over the role as the leading project of Ministry Of Education, Science and Technology (MEXT), Japan.

Using liquid Sn target has one major problem though, and that is high generation of debris. In this research, we are purposing to investigate the possibility of producing bulk nanoporous Sn target, to be used with CO₂ laser for EUVL. The result of producing bulk nanoporous Sn can be profitable in investigating the conversion rate with CO₂ laser in future research.

In the early years of integrated circuit fabrication, there were many challenges that need solving. The technology expands rapidly but scientists and researchers face numerous challenges in fabricating the smallest dimension. Comparatively speaking, we can build the largest building in the world but the same challenges do not apply in making the smallest building in the world, such as the block in an Integrated Circuit (IC). EUV lithography becomes a new dimension in technology especially for future semiconductor devices to fabricate the smallest integrated circuit, and commercially, the EUV lithography research becomes a leading prospect [3, 4]. Furthermore, there are still concerns about the source of lithography. In the technology of EUV lithography with alternative Laser-Produced Plasma (LPP), tin droplet is still found to be inferior in overcoming debris problem [5, 6]. In this research, the fabrication of solid-state powder of Sn, SnO₂ and Zn becomes ideal with bulk nanoporous condition.

The bulk nanoporous method is a means of getting low density porous material and also a good idea in getting low plasma density target. Through good control of the parameters, the sample is fabricated by compacting and sintering process [7, 8]. Sintering offers the flexibility of making the target into the desired shape. The porous form is obtained through a mixture of materials combined with other related parameters

such as pressure, temperature and material ratio. The compacting process is rather difficult for brittle material, as the material might collapse and crack during compacting or sintering process. Besides that, the production of Sn, SnO₂ and Zn is sintered to remove all other materials.

The electrical characterisation is important to be used as a starting point for further research. Each material has its own unique electrical path, where the porous structure might influence the conductivity of a material. The state of materials, namely solid, liquid and gaseous are commonly preferred, but in this condition low solid porous material is studied. The electrical conductivity from impedance analysis is used as valuable information. The parameter application might also influence the result of the analysis. The porous structure is the interesting part of the study because in certain situations it can display low path conductivity, but not good in terms of conductivity compatibility. The study of porous structure gives potential ideas for device application in electrical conductivity such as radio frequency identification (RFID), impedance and capacitance perspective.

Sample data collection involves controlling the identified ratio, pressure, time and temperature. The process of fabricating bulk nanoporous is not easy, where a number of critical conditions need identifying especially in controlling the parameters [9]. Even if the bulk nanoporous can be fabricated, contamination still becomes an issue. The XRD is chosen as a means of analysing this problem, even though it does not solve it. The phase formation of material is identified through XRD analysis. As for studying the morphology of material, SEM is used to identify the characteristics of bulk nanoporous through image formation. Moreover, the electrical impedance spectroscopy can justify the dielectric constant, impedance, and capacitance toward material. From the research,