NANOINDENTATION OF COPPER THIN FILM ON SILICON SUBSTRATES

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NANOINDENTATION OF COPPER THIN FILM ON SILICON SUBSTRATES

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DECLARATION

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LIST OF ABBREVIATIONS

MD	Molecular Dynamics
PCB	Printed Circuit Board
AFM	Atomic Force Microscopy
FCC	Face Centered Cubic
FE	Finite Element
LAMMPS	Large-Scale Atomic/Molecular Massively Parallel Simulator
OVITO	The Open Visualization Tool

ABSTRAK

Pada hari ini, metalisasi telah beralih kepada kuprum kerana kekonduksian elektrik dan haba yang tinggi, suhu lebur yang lebih tinggi, dan kadar resapan yang lebih rendah berbanding dengan logam lain. Dalam kajian ini, kaedah nanoindentation digunakan untuk mengkaji ciri mekanikal filem kuprum nipis dengan kedalaman lekukan skala nanometer. Ciri-ciri tersebut dikaji melalui dua pendekatan iaitu analisis eksperimen dan simulasi. Dua jenis filem kuprum iaitu kuprum PCB dan kuprum tulen diuji di makmal. Setiap sampel datang dengan ketebalan yang berbeza dan telah diuji pada 10 mata dengan parameter lekukan yang sama. Keputusan eksperimen menunjukkan bahawa kekerasan PCB kuprum lebih tinggi daripada kuprum tulen. Nilai modulus Young memberikan trend yang berbeza kerana PCB kuprum mempunyai nilai yang lebih rendah daripada kuprum tulen. Keputusan ini berbeza-beza kerana kedalaman penembusan dan jenis lapisan untuk kedua-dua sampel adalah berbeza. Simulasi dinamik molekul tiga dimensi (MD) juga digunakan untuk mengkaji nanoindentasi lapisan nipis tembaga pada substrat silikon. Potensi Lennard–Jones (LJ) digunakan untuk mensimulasikan sistem filem/substrat dengan menerangkan interaksi pada antara muka substrat filem. Simulasi diperiksa pada beberapa ketebalan berbeza sampel pemodelan dengan menggunakan Simulator Selari Besar-besaran Atom/Molekul Berskala Besar (LAMMPS). Alat Visualisasi Terbuka (OVITO) digunakan untuk menjana perwakilan tiga dimensi bagi simulasi. Keputusan yang diukur menunjukkan bahawa ketebalan yang lebih rendah akan memberikan kekerasan yang lebih besar bagi filem nipis kuprum. Substrat silikon akan menghasilkan kesan kecil pada daya pemuatan apabila sampel ditembusi. Beberapa penjelasan yang munasabah untuk pergantungan kedalaman kualiti kekerasan pada kedalaman lekukan skala nano ditawarkan dan dibincangkan.

ABSTRACT

In this day, metallization has shifted to copper because of its high electrical and thermal conductivity, greater melting temperature, and lower rate of diffusivity compared to other metals. In this study, nanoindentation method is used to examine the mechanical characteristics of thin copper film with nanometer-scale indentation depths. The characteristics is investigated by two approach which is experimental and simulation analysis. Two types of copper film which are copper PCB and pure copper are tested in the laboratory. Each sample comes with different thickness and been tested at 10 points with same indentation parameter. The experimental results showed that the hardness of copper PCB is higher than the pure copper. The Young's modulus value gives different trend as the copper PCB has lower value than the pure copper. This result is varied because the penetration depth and the type of layer for both sample is different. Three-dimensional molecular dynamic (MD) simulation is also being used to examine the nanoindentation of copper thin layer on silicon substrate. Lennard–Jones (LJ) potential is used to simulate the film/substrate system by describing the interaction at the film–substrate interface. The simulation is examined at few different thicknesses of the modelling samples by using the Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The Open Visualization Tool (OVITO) is used to generate the three-dimensional representation of the simulation. The results measured showed that the lower thickness will give greater hardness of the copper thin film. The silicon substrate will produced a small affect at the loading force when the sample is penetrated. Several plausible explanations for the depth dependence of hardness qualities at nano-scale indentation depths are offered and discussed.

CHAPTER 1
INTRODUCTION

1.1. Introduction

A few decades ago, a stress-strain curve created by an applied load was the most common technique used to determine the mechanical characteristics of materials. The properties must be analyzed especially for product build-up, process management, and material investigation. In 1970, an advanced technique known as indentation was developed, capable of providing various properties in a single test. Traditionally, micro-indentation is discovered to be useful for the characterization of thick films while simple indentation is found to be acceptable for the characterization of bulk materials. The advancement of nanoindentation has become the common technique for measuring material hardness and elastic modulus. The adversity for determining the mechanical properties for thin films has made this technique become the main choice as it can be handled on a tiny surface area for testing. Various range of mechanical characteristics can be determined by combining the application of modest loads, measuring the subsequent displacement, and estimating the contact area between the tip of the indenter and the sample. Furthermore, the increase in the production of thin films all around the world has made nanoindentation very important to determine the characterization of the materials. Copper was prominent for the materials' selection in the manufacture of electrical components due to its high strength, good conductivity and reliability. The characterization of the copper film's properties and its mechanism is decisive to obtain a good device. The application of nanoindentation is very favorable for manufacturers to test the properties of the copper films. However, there is some limitation to achieve the best result outcomes when the thickness of copper film involved the nanoscale unit. Nonetheless, the molecular dynamic (MD) and finite element (FE) simulation can support the nanoindentation technique to study the material properties. This type of computer simulation provides a larger scale from a small to a bigger number of atoms and gives a better understanding of the nanoindentation process.

1.2. Project Background

This project aims to determine hardness and Young's modulus of copper thin film on silicon substrate. Copper has been chosen in this study because of the special material properties and high demand in the electrical industry. As thin-film material has become important technology all around the world, the material characterization of the copper film must be very particular for the manufacturing of a reliable product. The mechanical properties of the copper thin film will be determined by the application of the nanoindentation technique. This technique is very famous as it gives the best practicability in the context of characterizing the mechanical properties of thin films. Up to now, nanoindentation is has been confined to indentation depths of less than a micrometer range. The advanced technology in the industry has pushed the nanoindentation technique to produce a higher precise measurement of thin film which will be measured on the nanometer scale. However, the development of the device system made it necessary for the nanoindentation technique to characterize thin film using high resolution and depth-sensitive indentation. The involvement of the computer simulation with indentation studies in nanometer-scale has inspired the growth of numbers of the simulation model. The development of the simulation model provides better insight to understand the mechanical characteristics and mechanisms. This paper will focus on the molecular dynamic method which will use LAMMPS code while an experiment also will be conducted to provide real data which can support the outcome of the results of the study. Different applied loads and penetration depths will be implemented in this research study. The results from the computer simulation will be used to compare with the real experimental data. This study is expected to reveal the hardness of copper thin films on silicon substrates from various thicknesses.

1.3. Problem Statement

Metal films have become an important material in electrical industries, especially semiconductor technology. The greater electromigration resistance and low resistivity have made copper become the preferred connection material. It is critical to understand the mechanical characteristics and deformation processes at the first step. There are many techniques to evaluate the properties of a copper thin film. However, nanoindentation is likely to be the best technique as it can measure in order of nanometers. Therefore, this paper will present the output of nanoindentation from various thicknesses of copper thin film on a silicon substrate.

1.4. Objectives

1. To determine the hardness and Young's modulus of copper thin film on silicon substrates.
2. To achieve a better understanding of the material properties by using the nanoindentation technique.
3. To have a better vision of the research by validation of the results using molecular dynamic simulation and subsequently comparing with the experimental data.

1.5. Scope Of Work

This research project involves both computer simulation and hands-on experiments to study the mechanical properties of copper thin film on silicon substrates. Various thickness of copper film and substrates material will be considered in the experiment. The nanoindentation test will run with an increasing load and penetration depth. Then, the process will be simulated by using LAMMPS code and the results can give the prediction of Young's modulus and hardness of the copper film.

1.6. Thesis Outline

This thesis report will have five chapters, beginning with Chapter 1, which discusses the project's introduction. This chapter examines the underlying research, problem statement, objectives and scope of the nanoindentation.

The second chapter provides a literature review based on the published research articles associated with this project. The papers utilised in this research were obtained from the online source in order to investigate previous studies and gaps in analysis. The issues and answers discovered in prior research are considered.

In the third chapter, the methodology for the study will be discussed. This chapter will be explained on how to do the laboratory experiment of nanoindentation test for the thin film. This section also involves the design simulation with proper elaboration.

In the next chapter, the nanoindentation of copper thin films on silicon substrates will be discussed as a result of the project. The results will be included from the experimental and simulation analysis.

In the final chapter of this research project, a conclusion and summary of the findings acquired from the previous chapters are presented. The findings of the study, as well as the researchers' suggestions on how things may be improved further in the future, have also been provided.

CHAPTER 2
LITERATURE REVIEW

2.1. Introduction

Thin films have become such an integral part of human existence that it is difficult to identify a field of endeavour in which they are not present. Semiconductor production is one of the industries where thin films are not only beneficial, but also the main manufacturing technique. When fabricating an integrated circuit, thin sheets are deposited over a highly flat substrate, which is typically composed of silicon. Each microscopic device is constructed from the connectivity of thin film layers that have been doped differently, and the interface between devices is controlled by metallic thin-film layers, often composed of aluminium or copper.

The nanoscale mechanical characteristics of a material are crucial to the advancement of nanoscience and technology. Nanoindentation is the most applicable method for assessing the mechanical properties of nanometer-scale thin films and surfaces. Hence, this study is to examine the hardness of copper thin film on silicon substrate by nanoindentation method.

2.2. Properties Of Copper

Copper is considered to be the first metal to be worked by humans over the course of history. A wide range of manufacturing processes make use of copper. Copper is a metal that is highly sought after by manufacturers due to its malleability, ease of machining, and excellent conductivity. These qualities have led to copper's status as the industry's most popular metal. The arrangement of copper atoms in solid copper is known as a face-centered-cubic (FCC) configuration as shown in Figure 2.1. This arrangement may be used to characterise solid copper. Copper has great electrical and thermal conductivity, is magnetic in general, and has outstanding formability and strength. It is also extremely resistant to corrosion and fatigue. At the present day, copper is utilised in the construction of buildings, the generation and transmission of electrical power, the manufacturing of electronic products, as well as the creation of industrial machinery and transportation vehicles (John Emsley, 2011).

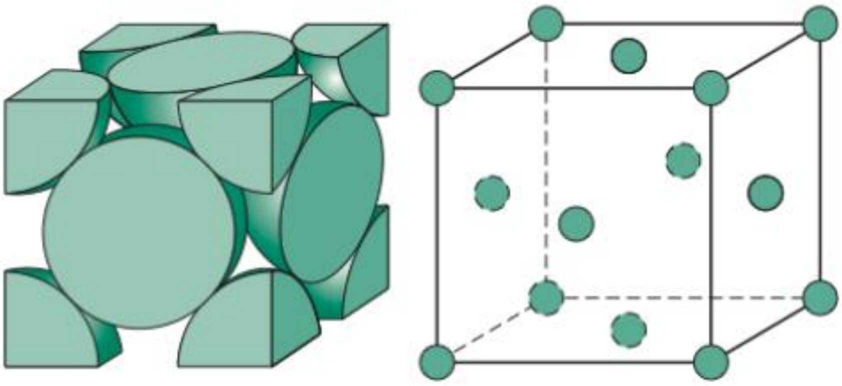

Figure 2.1: The geometry model of the indentation tool using MD simulation (Peng et al., 2010)

Table 2.1-2.6 show the mechanical properties, thermal, electrical, miscellaneous, and microstructural properties for the copper material (Member et al., 2007).

Table 2.1: Mechanical properties of Copper, Cu

Mechanical Properties	
Modulus of Elasticity	110 GPa
Bulk Modulus	140 GPa
Tensile Strength, Yield	33.3 MPa
Elongation at Break	60%
Poisson's Ratio	0.343
Shear Modulus	46 GPa
Hardness, Vickers	369 Mpa

Table 2.2 Thermal properties of Copper, Cu

Thermal Properties	
Specific Heat Capacity	0.385 J/g-°C
Melting Point	385 W/m-k
Thermal Expansion	1083.2-1083.6°C
Thermal Conductivity	(25°C) 16.5 $\mu m.m^{-1}.K^{-1}$

Table 2.3 Electrical properties of Copper, Cu

Electrical properties	
Electrical Resistivity	1.7e-006 ohm-cm

Table 2.4 Miscellaneous properties of Copper, Cu

Miscellaneous properties	
Grain Boundary Energy	625mJ/m^2

Stacking Fault Energy	45 mJ/m^2
Twin Boundary Energy	24 mJ/m^2

Table 2.5 Microstructural properties of Copper, Cu

Microstructure	
Crystal Structure	Face Centered Cubic
Atomic Radius	1.35 Å
Atomic number	29
Atomic weight	63.546 g·mol^{-1}
Electron configuration	$1S^2\ 2S^2\ 2P^6\ 3S^2\ 3P^6\ 3D^{10}\ 4S^1$

2.3. Hardness Properties

A material's hardness is its resistance to localised plastic deformation. Deformation is caused by a significant number of dislocation movements, edge and screw dislocations are prevalent in crystalline metals (D. Hull & D.J. Bacon, 2011). A tiny indenter with a predetermined load can be used to determine a material's hardness by penetrating the surface of the material under controlled conditions. The hardness of a material is determined by comparing the indentation load to the remaining indents on the surface or projected area (Zhang et al., 2011). According to hardness theory, softer materials produce indents that are deeper and bigger and have lower hardness index numbers. Aside from that, hardness testing is widely employed since it is easy and affordable compared to other mechanical testing methods. The results of the hardness test can provide an approximation number of the material's mechanical characteristics, including the tensile strength of the material. Vickers, Rockwell, Brinell, Mohs, Shore, and Knoop are the six most often used hardness tests. However, the test is depending on the type of material to be examine.

2.4. Strengthening Of Thin Film

The enhancement of the mechanical characteristics of metals has always been and will continue to be a primary area of focus for metallurgists and material science engineers. In most cases, increasing the hardness of a metal requires reducing its ability to be formed. The literature survey from past research paper showed that there are few techniques had been conducted to improve mechanical strength and get the best quality of the thin film. The decrease of grain size, the strengthening of solid solutions, and the strain hardening of materials are three well-known phenomena that contribute to strengthening.

However, thin films are strengthened in a fundamentally different manner than bulk materials. For instance, in nanometer regime thin films, solid solution hardening is not possible because impurities tend to migrate to the grain boundary area. Carbon impurities, for example, frequently permeate outside the grain boundaries in electrodeposited nanocrystalline nickel. As preventing dislocation motion is still the primary target of the majority of thin film hardening processes, the hall-petch connection still remains true for thin films (M.D. Merz & S.D. Dahlgren, 1975).

The majority of the research was focused on producing high-strength copper thin film albeit at the sacrifice of conductivity. In other research, a method was come up for depositing greater strength and high conductivity copper thin films on various silicon substrates at room temperature. This research suggests a method for depositing high strength and high conductivity copper thin films on various silicon substrates at room temperature. Cu (100) and Cu (111) single crystals were developed respectively on Si (100) and Si (110) substrates. Due to low twin border energy and a rapid deposition rate, single-crystal Cu (111) films contain a high density of growth twins aligned parallel to the substrate surface. This research paper covered various techniques to demonstrate that the increase in hardness of thin films comes from the greater density twins. The creation of growth twins is described, as well as their functions in increasing the mechanical strength of Cu films while preserving low resistivity. Focusing on the nanoindentation, this research was performed using a Ficherscope HM2000Xyp hardness tester. The hardness was assessed for each sample at an indentation depth of a certain distance and interval, with an array of 9 indentations were performed for each indentation depth. From the results obtained, nanoindentation reveals that copper thin films with high-density growth twins have very strong hardness. This research suggests that twin barriers might be a highly successful method for generating high strength and high electrical conductivity metallic alloys (Member et al., 2007).

2.5. Nanoindentation From Submicron To Nano-Scale

The nanoscale mechanical characteristics of a material are crucial to the advancement of nanoscience and technology (Jeng et al.,2012). Nanoindentation is a simple and effective method for assessing the mechanical characteristics of thin films and surfaces in the nanoscale range. Nanoindentation has thus far been confined to penetration depths of less than a micrometer. However, there is a growing demand for nanoindentation techniques that can figure out the mechanical characteristics of thin films at nanometer-scale indentation depths. Due to the lower electrical resistivity and higher electromigration resistance, copper is often chosen rather than aluminium as the connection material in integrated circuits and other electronic components to meet the requirements for high transmission (Hu & Harper, 1998). In nanoindentation experiments performed at the depths in the sub-micrometer regime, a size-dependent phenomenon has been discovered in experimental research. (Peng et al., 2010) investigated the nanoindentation of an aluminium thin layer on a silicon substrate using three-dimensional molecular dynamic simulation. This research aims to determine the hardness and Young's modulus of thin copper sheets using nanoindentation at thicknesses ranging from deep-submicron to nanoscale. Copper films of various thicknesses were deposited on a single crystal silicon wafer with a (100) orientation and a polymethylmethacrylate (PMMA) coating, respectively. A soft film on a hard substrate and its vice versa have their system properties tested and discussed. The substrate impact is negligible if the indentation depth is less than 20% of the thin film thickness. The substrate impact is usually important, hence the hard film on the soft substrate should be handled as a system in indentation. The research also reveals that thin coatings with thickness less than 100nm have a significant indentation size influence.

2.6. Nanoindentation Round Robin

The standardization of nanoindentation for hard films has evolved faster than that for soft films (Read et al., 2007). This is due to the hardness characterization is customary for hard coatings but not for electrical conductors and dielectrics. This research paper’s objective is to aid in the standardizing process of the indentation. The classic study by(D. Tabor, 1951) suggests that the hardness should be 3 times the stress attained in the tensile test at a plastic strain of roughly 8%. This conclusion holds for both nanoindentation and more standard hardness testing. Under the aegis of the American Society for Testing and Materials, a substantial and helpful collection of standard test techniques has been developed (ASTM). Efforts to standardize nanoindentation using standard ASTM techniques are currently underway. The standard test procedure includes a statement of repeatability and reproducibility which both are linked to the accuracy of the test procedure. The technique for assessing a test's correctness requires information about the "actual value" of the feature being evaluated, which is often unavailable. The predicted distribution of findings produced under a limited set of test settings, such as one instrument in one laboratory, is referred to as repeatability. Reproducibility is the predicted distribution of test findings under a more generic set of test settings, such as similar instruments in different laboratories. Both nanoindentation and more traditional hardness tests support this finding. Efforts are presently ongoing to standardize nanoindentation using conventional ASTM procedures. The analysis was unable to pinpoint a possible cause of uncertainty. This study has enough data to look at the impacts of numerous critical variables, including the instrument manufacturers, the test and analysis methodologies utilized, the state of the indentation tip, and the period since instrument calibration, one at a time. These factors did not have any statistically significant influence. Certain specimens, such as quartz and aluminium single crystals, are used in the calibration procedures for these devices. It's usually considered that these specimens are consistent enough that devices traditionally calibrated with them would work identically. This assumption may be called into doubt by the current investigation. The diversity in indentation tip forms, which are not effectively adjusted by existing procedures for determining the tip area function, cannot be ruled out as a cause of variance in the current study's results.

2.7. Nanoindentation By Molecular Dynamic (Md) Simulation

The research in this field is by (Peng et al., 2010) who studied the molecular dynamic of nanoindentation for aluminium thin film. Nanoindentation is said to be a popular method for the characterization of the mechanical characteristics of thin films and bulk materials(D.E. Kramer et al., 2001). However, accurate control of the penetration depth, the extremely tiny indentation stress, and the indented areas' measurements are all the challenges for this test. In bioscience, material science, and technology, molecular dynamic (MD) simulation is a potential tool for studying material properties. The interface of thin films and substrates in most FE simulation methods was explained by the friction contact model, although it is not suitable for nanoscale modelling. The fundamental atomic structure of matter is ignored, and a repeated and various mass density is used instead. Some of the other previous studies used the MD approach to replicate the indentation process but they were all confined to modelling monolithic material films. Then, a film–substrate system is modelled in this research. The indentation analysis model is shown in Figure 2.2. The interaction between an aluminium thin layer and a silicon substrate is described by the LJ potential which the hardness of the extremely thin coating on the substrate and the system deformation during the process was investigated. The nanoindentation was found out that the hardness of the film increases when the indentation speed is higher.

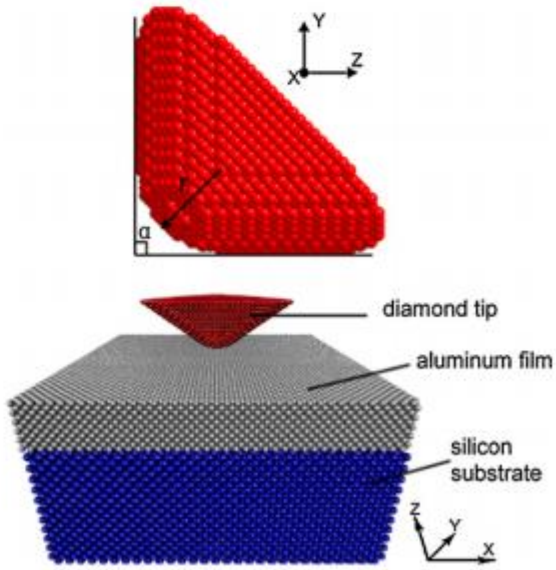

Figure 2.2: The geometry model of the indentation tool using MD simulation (Peng et al., 2010)

2.8. Nanoindentation Of Copper Film

A contemporaneous multiscale approach is used in a study by (Ng et al., 2011)to analyze the nanoindentation of a copper thin film. Molecular dynamics (MD) simulation has been the favored choice for exact material modelling at nanoscale scales. By using complete atomistic models that incorporate multiple empirical interatomic potentials, nanoindentation has been successfully deformed(D. Christopher et al., 2001). Despite that, the number of atoms is limited for the MD because to handle billions of atoms at micron-scale was confined for the computational power. A subversive way was come out by multiscale method to overcome the limitation of atom number which the atomistic and continuum will be merged. The meshless method in the multiscale is yet to bis e perfect even though they are proven to settle some of the engineering issues. This research emphasizes the analysis of nanoindentation for the copper thin film using the multiscale method. They can validate the correctness of the already developed 2D multiscale approach by examining the load vs indentation depth curve for the models. From the results, full atomistic simulation was compared with the meshless formulation which reveals that the multiscale method can simulate nanoindentation accurately.

2.9. Different Between Bulk Material and Thin Film

It is important to understand the mechanical characterization of the copper thin films on silicon substrates. Various investigations have revealed that the mechanical characteristics of thin metallic films differ significantly from the bulk material due to the size effect(G. Dehm et al., 2002). The authors' study of the nanoindentation response of thin aluminium-silicon lines is the sole experimental investigation on this subject that they are aware of. The study found that the lower the line width, the plastic compliance of the lines will rise. This nature cannot be represented by continuous finite element method (FEM) computations that do not take into account the researched object's length scale. The results of the instrumented nanoindentation of patterned copper lines on a silicon substrate are presented in this publication. The experiment's purpose is to investigate the relationship between the mechanical properties of a line and its distance from its edge. Besides measuring the width of a family of lines (Y. Choi et al., 2003), they altered the distance between the indented center and the line's edge. The results show that as the distance between the indented center and the strip edge decreases, the indentation of copper lines increases, beginning at a certain distance. The typical behaviour of material near the edge was exposed using AFM scans. On the nanoscale scale, necking and fracturing of the thin walls separating the indent from the line edge and inward relaxing of the walls during unloading were observed. The reported results are explained using the elastoplastic indentation model.

CHAPTER 3
METHODOLOGY

3.1. Introduction

This project determines the hardness of copper thin film on silicon by using nanoindentation technique from experimental and molecular dynamic (MD) simulation. This chapter provides a summary of the methods that were used to carry out nanoindentation tests that were conducted earlier in the study. The purpose of this chapter is to guarantee that the project is well-organized and properly handled. As a result, this chapter provides a simpler phase by phase approach, which allows for the discovery of difficulties at an early stage, hence preventing certain failures. This project will focus on nanoindentation which also had been a common technique for measuring the hardness of a material.

3.2. Experimental Procedures

The hardness of the material will be conducted by both methods which are experimental and simulation of molecular dynamics. The hardness of the material can be achieved by dividing the area of nanoindentation with the load of the indenter. The diagram or the mechanism of the nanoindenter is shown in Figure 3.1.

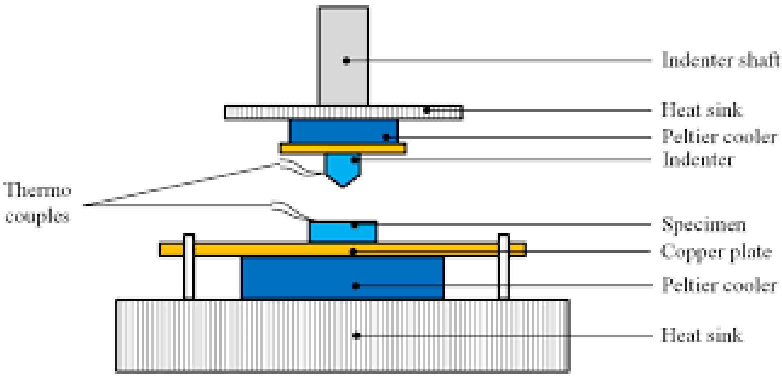

Figure 3.1: Diagram of the nanoindenter (S. Wang & Zhao, 2020)

Indentation in the micrometer range may go through the thickness of the material onto the substrate, resulting in a muddled value for the measured hardness of the film and substrate. Hence, the indentation in nanometers scale has been the preferred method. In the experimental study, hardness measurements were conducted using the

NanoTest machine by Micro Materials as shown in Figure 3.3. Two different types of thin film specimens as shown in Figure 3.2 which are pure copper and copper PCB board had been tested. The thickness of pure copper is approximately 0.792mm and copper PCB board is 0.805mm. Berkovich type of indenter tip was used in this experiment. The specimen was conducted with indentation load applied 100mN with a retraction distance of 15µm. The indentation speed of the experiment 5.0 mN/s for the loading and unloading rate. Ten indentation points are chosen in both specimens. The results of the indentation were presented in every point and the average of all points respectively.

(a) Copper PCB

(b) Pure copper

Figure 3.2: Experiment samples for (a) copper PCB and (b) Pure copper

The tip radius, R of the Berkovich indenter will have an impact on the relationship between the indentation load, P and the penetration depth, h at the beginning of elastic deformation occurred, where

$$P = \frac{4}{3} E' \cdot h^{\frac{3}{2}} \cdot R^{\frac{1}{2}}$$

$$E' = \left(\frac{1 - v_f^2}{E_f} + \frac{1 - v_{ind}^2}{E_{ind}} \right)^{-1}$$

where E’ and ν are Young’s modulus and Poisson’s ratio, respectively, and the subscripts, ‘f’ and ‘ind’ refer to the film and the indentor, respectively.

Figure 3.3: NanoTest machine

To compute indentation hardness, all deformations during the unloading of the indenter are considered to be elastic. The following is a step-by-step description of the indentation procedure:

1. Press the indenter onto the specimen with the desired load.
2. Elastic and plastic deformation of the specimen will cause displacements.
3. The indenter is removed from the specimen.
4. The deformation of the specimen will be recovered.

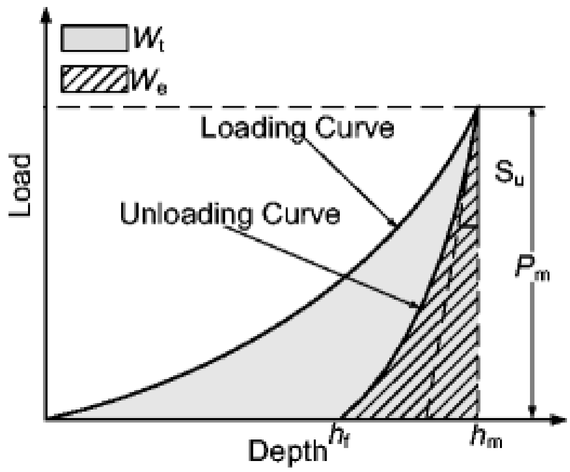

Figure 3.4: Schematic representation of indentation hardness curve(Ma et al., 2016)

As stated before, the hardness of indentation can be known by dividing the area of nanoindentation by the load of the indenter.

$$H_{IT} = \frac{P_{max}}{A_c}$$

where, $A_c = f(h_c)$

h_c is the height of contact of the indenter with the specimen and given by,

$$h_c = h_{max} - \varepsilon(h_{max} - h_i)$$

ε is the function of the shape of the indentation tip and the values are presented in Table 3.1,

Table 3.1: Various indenter tip value

Indenter Shape	ε
Flat Punch	1.0000
Cone	0.7268
Sphere	0.7500
Paraboloid	0.7500

The value of ‘f’ is specified in International standards for each type of indenter (Member et al., 2007). This experiment used Berkovich indenter and the value of ‘f’ is 24.5 which the tip has the same projected area to-depth ratio as the Vickers indenter.

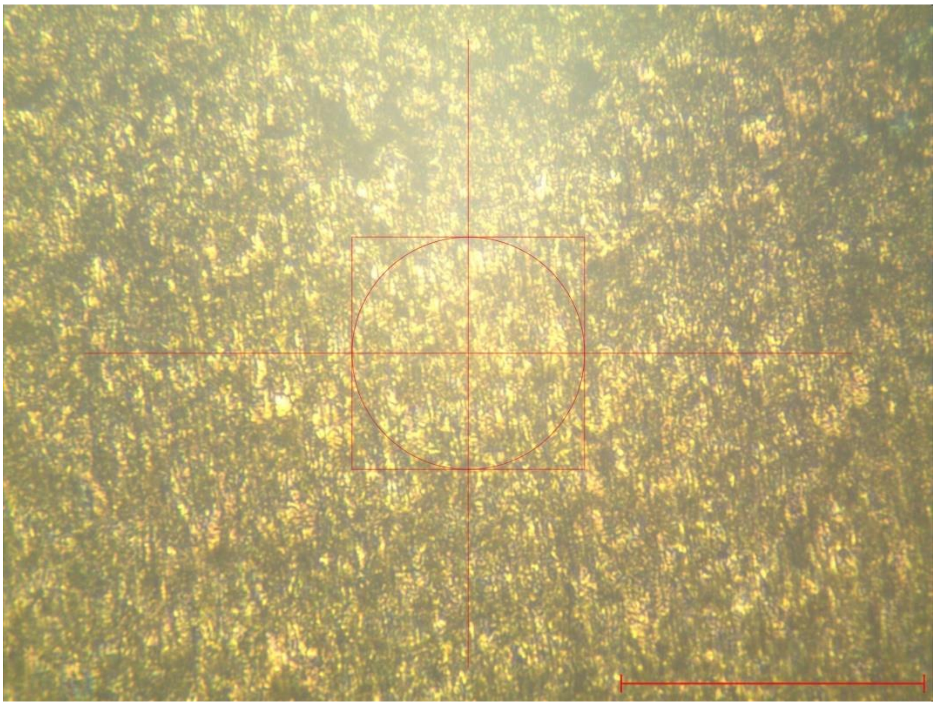

Figure 3.5: AFM image on sample to be indent

3.3. Molecular Dynamic (MD) simulation

Besides the experimental works, the simulation of the nanoindentation process will be carried out to study the mechanical properties of copper thin film on silicon substrates. In the available study, some works already study nanoindentation by using finite element (FE) simulation. FE analysis is a continuum mechanics approach that ignores the underlying atomic structure of matter entirely in favour of a continuous and differentiable mass density. Hence, it was said to be less suitable for the nanoscale simulation. The FE analysis is commonly used to estimate the deformation, stress distribution, and the indenter’s force versus displacement responses.

In this project, molecular dynamic (MD) simulation will be implemented which has been widely used to study the material characteristics. MD is the preferred method for large molecules as the evolution of computer simulation develops the scale from thousands to millions of atoms. (T. Iizuka et al., 2001) and some recent works employed MD simulation to investigate the relationship between thin film porosity and hardness on a substrate. Recent studies help to understand the nanoindentation, but all the mechanical properties of the thin film were not well investigated. A film–substrate system is described in this project, with the LJ potential employed to characterize the interaction between the copper thin film and the silicon substrate. The energy between two atoms is given by the following equation for LJ potential.

$$E_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]$$

Where E_{ij} is a pair potential energy between atom i and j. ε_{ij} is the coefficient of depth energy and σ_{ij} is equilibrium distance. These two subscripts' parameters is only for a one type of atoms.

LAMMPS is used to create input scripts, which are then used in this work to carry out MD simulations. Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) is an atomistic modelling code for doing classical molecular dynamics simulations. It comes with a set of pre-built instructions. The command prompt software is used to execute input scripts, which are created in the LAMMPS programming language. Two crucial output files are generated when a simulation is executed. All of the parameters of the system, including its pressure, volume, temperature as well as the force acting on a group of atoms and the time that was computed for the simulation, are written down to the log file. The second file is known as the dump file, and it stores both the locations of atoms at certain time steps as well as the attributes of atoms that were computed throughout the run. To generate a three-dimensional representation of the simulation, visualisation tools which is OVITO use the dump file as their source data.

Figure 3.6 shows the schematic diagram representing nanoindentation simulation of copper thin film on a silicon substrate. A few different thicknesses of the thin film are evaluated.

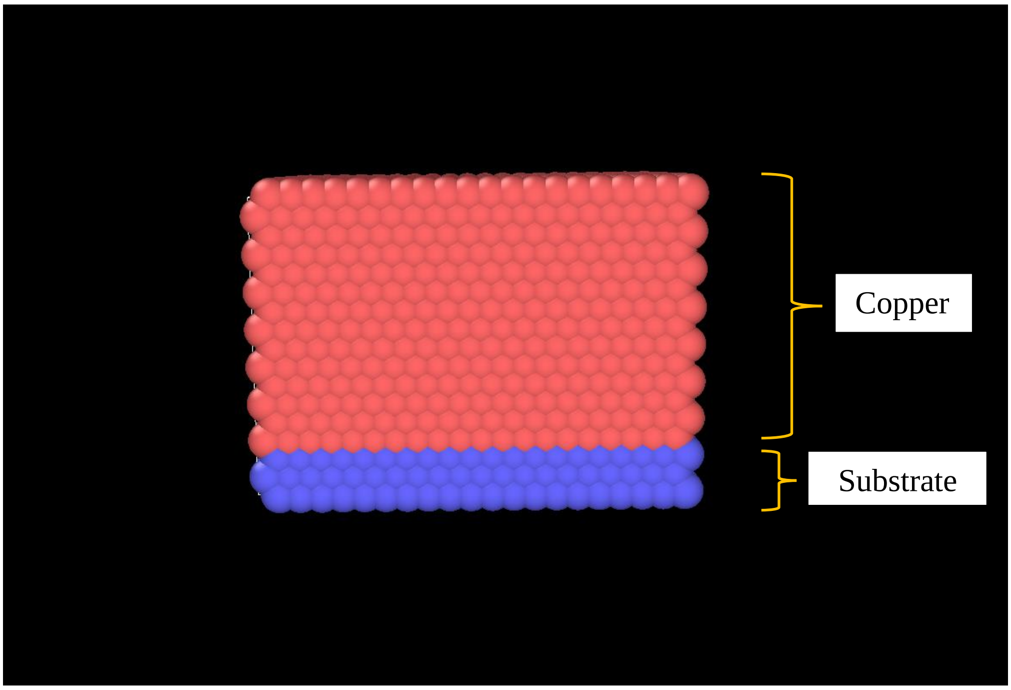

Figure 3.6: Schematic diagram of a nanoindentation simulation

In this study, a spherical indenter is used and placed at the top of the specimen regime. Then, the indenter is set at the center and moves with steady velocity onto the sample surface. Interactions between the substrate and spherical indenter with a radius of R follow:

$$V(r) = \begin{cases} \frac{K}{3}(r-R)^3, & r < R \\ 0, & r \geq R \end{cases}$$

Where r is the distance between the indenter and the sample atoms. K is a force constant in which the value is 10 eV/Å^3. This simulation model is not the same sample to the nanoindentation by the experiment. However, the simulation is said to provide outcomes that are equivalent to the experiment (Mordehai et al., 2011). The value of LJ potentials for copper is included in the input parameter of the simulation. Four different thickness which is 12nm, 20nm, 30nm, 40nm will be observed. The Open Visualization Tool (OVITO) are used to analyze and visualize data achieved from the simulation of the nanoindentation (Stukowski, 2010). The analysis and visualization of the data to identify the dislocation of the atoms is conducted using Dislocation Extraction Algorithm (DXA).

The hardness,H is measured by the maximum indentation load Pmax divided by the anticipated contact area Ac, which is given by the following equation, (Peng et al., 2010).

$$H = \frac{P_{max}}{A_c}$$

The geometry of the indenter tip, which may be represented as equation below, can be used to roughly determine the projected contact area.

$$A_c = \frac{3\sqrt{3}}{2} h^2$$

where h is indentation depth.

In addition, reduced modulus can be calculated from the simulation to indicate the elastic deformation that take place from the indenter and the sample tested(Crocker, 2007).

$$\frac{1}{E^*} = \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'}$$

Where,

E* = Reduce Modulus
E = Modulus of the thin film
E' = Modulus of indenter
ν = Poisson's ratio of the thin film
ν' = Poisson's ratio of the indenter

According to the geometrical similarity principle, for every given a/d or h/d ratio, the deformation fields should take on an invariant geometric shape (Mazeran et al., n.d.). In this paper, some modifications to a straight forward method developed by (Xiao Hu & B.R. Lawn, 1998) in the past for spherical indentation by formulating the modulus E as power-law functions,

$$E = E_s \left(\frac{E_f}{E_s}\right)^L$$

Where E is the modulus with the subscript s as the substrate, f as the film and L is spatial functions L= L(h/d). In this formulation, the geometry terms are decoupled from the material terms.

CHAPTER 4
RESULTS & DISCUSSION

4.1. Introduction

This chapter summarises the findings from experiments and techniques used in accordance with the procedures outlined in chapter 3 to get the results. The outcomes of the experiment's nanoindentation tests for several types of copper thin films are addressed in the results. All the data collected are tabulated, analyzed, and supported by images obtained by AFM analysis.

4.2. Experimental Result

4.2.1. Result for Copper PCB sample

Figure 4.1 represents the AFM image of the indentation on a copper PCB board. The proposed analytical techniques compute the hardness and elastic modulus by averaging the results of ten indentations made on film sample under the same testing circumstances. The average of the hardness and other parameters for copper thin film are shown in Table 4.1. The penetration depth for all the points in the experiment is measured in nanoscale which improve the nanoindentation results.

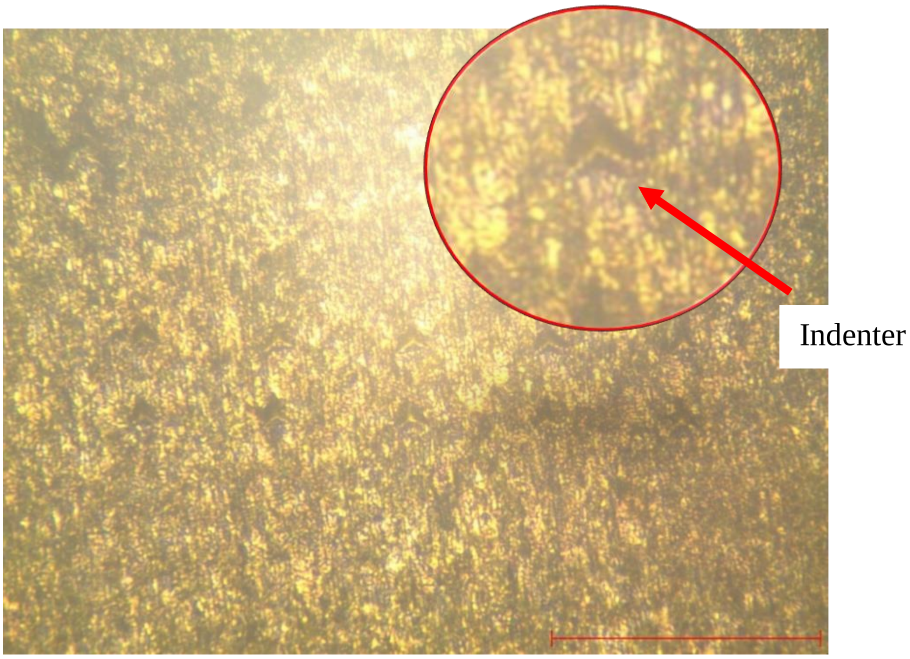

Figure 4.1: AFM image of Berkovich indenter on copper PCB sample

Table 4.1 Analysis result for copper PCB film

Analysis Results	
Maximum Depth (nm)	1739.96 ± 133.19
Maximum Load (mN)	100.010 ± 0.000
Plastic Depth (nm)	1617.14 ± 133.99
Hardness (GPa)	1.58805 ± 0.243
Reduced Modulus (GPa)	65.76485 ± 4.895
Elastic Recovery Parameter	0.0764 ± 0.007
Contact Compliance (nm/mN)	1.64 ± 0.03

The average hardness for the copper PCB film that had been measured at ten different points is 1.58805 GPa (Table 4.1). The hardness is measured using Oliver and Pharr method (Smallman & Ngan, 2014). The maximum depth from the nanoindentation is 1739.96 nm and the maximum load applied on the copper thin film is 100.01mN. The load increase as the penetration depth going deeper until the critical force was shown and the force returned to its original condition. Indentation simulations with displacement control frequently exhibit this behaviour. The reduce modulus is 65.76 GPa which indicates the elastic deformation that happens in the thin film and indenter.

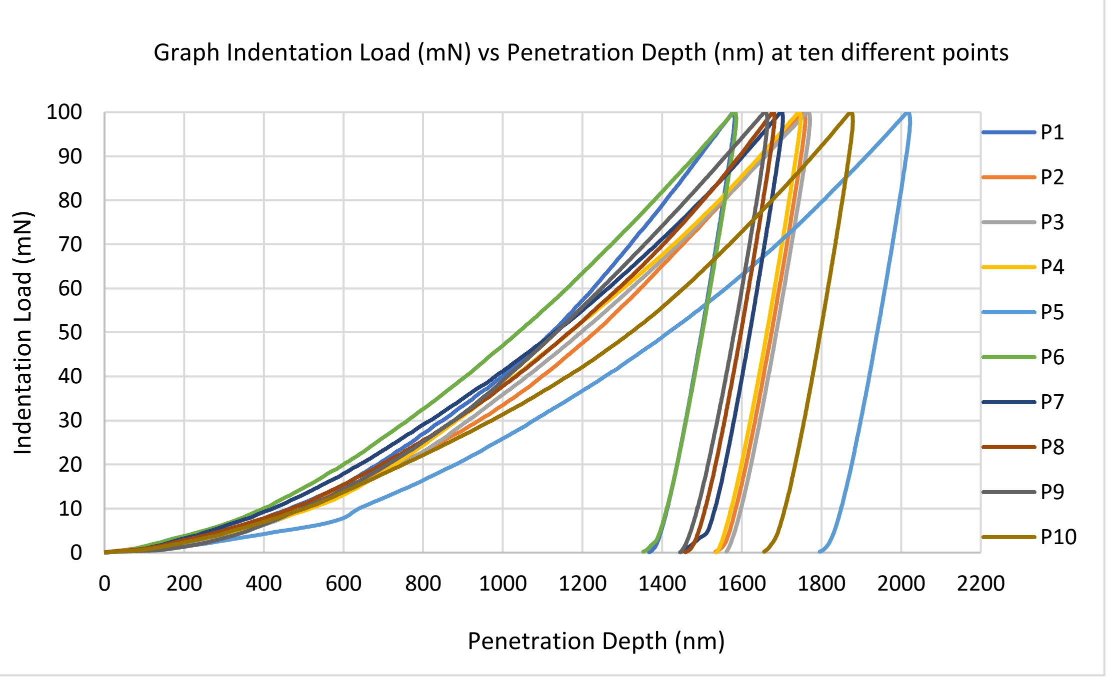

Figure 4.2: Graph indentation load (mN) vs penetration depth (nm)

The indentation load versus penetration depth for copper PCB film was presented in the Figure 4.2. All the ten points of nanoindentation were tested and plotted in the figure. The trend for the results shows the loading and unloading rated during the experiment. The load begins the indentation process with an attracting force. Then it starts to build up and takes control. The maximum load imposed at 100 mN and uniformly applied to all the nanoindentation points. The indenter starts to return and the force dramatically decreases after the maximum indentation depth is attained and re-equilibrium is carried out. However, the maximum penetration depth shows different values at each point.

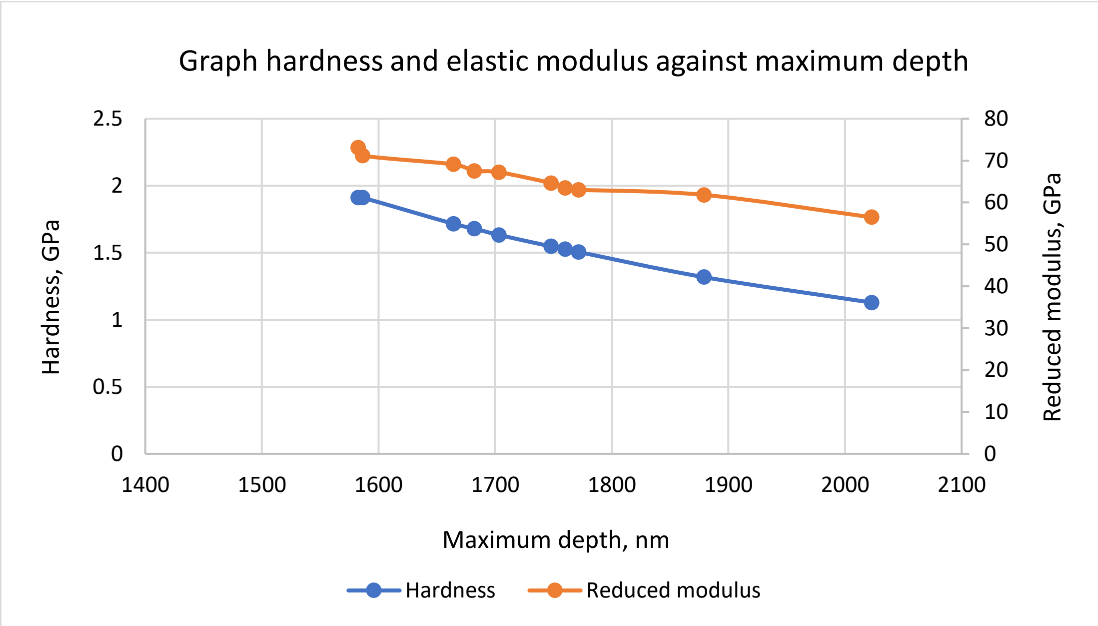

Figure 4.3: Graph hardness and elastic modulus against maximum depth at ten different point

From Figure 4.3, it represents the hardness and elastic modulus of the copper PCB against the maximum depth at ten different points. From the graph, we can see that the hardness of the sample is decreases when the maximum depth increases between the point indents. The point which has the highest value of the hardness, 1.913 GPa was obtained at the maximum depth, 1582.464 nm. For the elastic modulus, the highest value is 73.109 GPa which observed at the same maximum point.

Table 4.2: Result of nanoindentation at ten different points

No.	Max Depth (nm)	Hardness (GPa)	Er (GPa)
1	1582.464	1.913	73.109
2	1586.199	1.911	71.190

3	1664.307	1.716	69.107
4	1682.148	1.680	67.563
5	1703.333	1.633	67.232
6	1747.811	1.548	64.642
7	1760.009	1.527	63.474
8	1771.449	1.506	63.026
9	1879.077	1.318	61.825
10	2022.800	1.129	56.479

4.2.2. Result of Pure Copper sample

Figure 4.4 represents the AFM image of the indentation on a pure copper film. The specimen was indented with the same input parameter from the previous sample at ten different points. The average of the hardness and other parameters for copper thin film are shown in the Table 4.3. The penetration depth for all the points in the experiment is measured in nanoscale which improve the nanoindentation results.

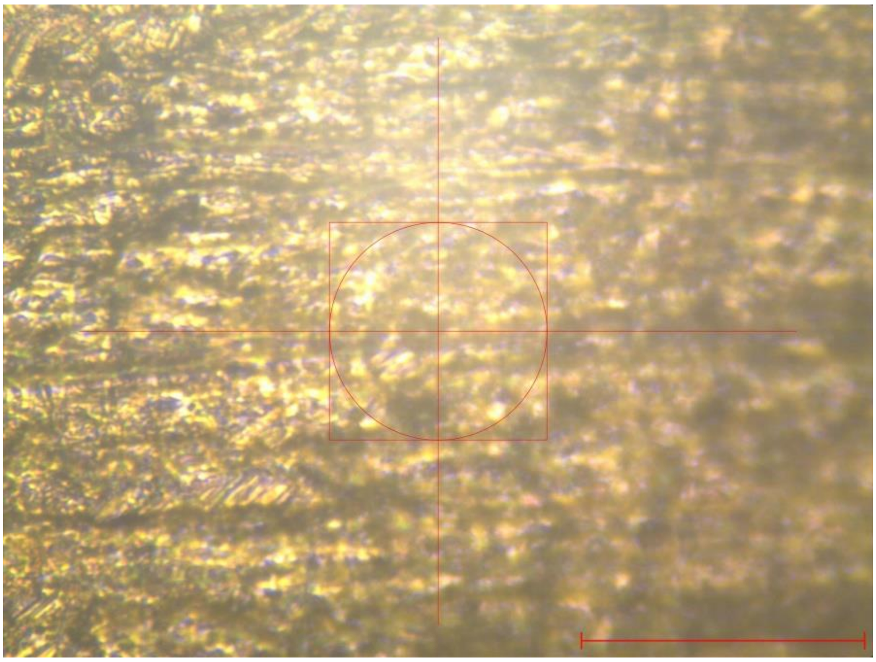

Figure 4.4: AFM image of Berkovich indenter on pure copper film

Table 4.3 Analysis of result for pure copper film

Analysis Results	
Maximum Depth (nm)	1942.70 ±284.23
Maximum Load (mN)	100.010 ± 0.000
Plastic Depth (nm)	1901.16 ± 284.14
Hardness (GPa)	1.19816 ± 0.348