DEVELOPMENT OF TERNARY Ni-Ag-P AND Ni-Cu-P USING ELECTROLESS COATING ON COPPER SUBSTRATE

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by

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LIST OF ABBREVIATIONS

3D	Three-dimensional
AFM	Atomic Force Microscopy
CTAB	Cetyltrimethyl Ammonium Bromide
EDX	Energy Dispersive X-ray
EN	Electroless Nickel
Ni-Ag-P	Nickel-argentum-phosphorus
Ni-B	Nickel-boron
Ni-Co-P	Nickel-cobalt-phosphorus
Ni-Cu-P	Nickel-copper-phosphorus
Ni-Cu-P-PTFE	Nickel-copper-phosphorus-polytetrafluoroethylene
Ni-Mo-P	Nickel-molybdenum-phosphorus
Ni-N	Nickel-nitrogen
Ni-P	Nickel-phosphorus
Ni-P-PTFE	Nickel-phosphorus-polytetrafluoroethylene
Ni-Sn-P	Nickel-stannous-phosphorus
Ni-W-P	Nickel-tungsten-phosphorus
Ni-Zn-P	Nickel-zinc-phosphorus
Ni-Zn-P-TiO2	Nickel-zinc-phosphorus-titanium dioxide
OM	Optical Microscope
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscope
TIM	Thermal Interface Media
XRD	X-ray Diffraction

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
µm	Micrometer
at.%	Atomic percentage
C_p	Correction factor
d	Diameter
D	Distance
dm^2	Square decimeter
d_p	Spacing between diffracting planes
g	Gram
h	Hour
HK	Knoop hardness
kg	Kilogram
kgf	Kilogram-force
kV	Kilovolt
L	Liter
L_i	Length
L_N	Load normal
m	Meter
M	Molar concentration
mg	Milligram
mm	Milimeter
N	Newton

n	The order of reflection
nm	Nanometer
P	Load
pm	picometer
r	Radius
t	Thickness
W	Mass
wt.%	Weight percentage
θ	Angle
λ	Wavelength of x-rays beam

PEMBANGUNAN TERNARI Ni-Ag-P DAN Ni-Cu-P MENGGUNAKAN SADURAN TANPA ELEKTRIK KE ATAS SUBSTRAT KUPRUM

ABSTRAK

Pada masa ini, ujian fungsi ke atas peranti dalam industri semikonduktor menggunakan media perantaraan haba, namun ia kadang kala menyebabkan kecacatan kosmetik seperti kekotoran atau calar. Satu penyelesaian yang mungkin untuk menghapuskan kecacatan yang tidak diingini ini adalah dengan menambahbaik saduran *nickel-phosphorus* (Ni-P) yg digunakan di atas *test chuck* dari segi keupayaan untuk memindahkan haba dengan cekap dan dengan itu mengelakkan penggunaan media perantaraan haba. Pemendapan perak (Ag) dan kuprum (Cu) ke dalam saduran Ni-P dijangka dapat meningkatkan kekonduksian haba saduran Ni-P tanpa mengorbankan ciri-ciri saduran yang lain; kekasaran permukaan, ketebalan, kekerasan dan rintangan haus. Kerja-kerja penyaduran Ni-P telah dijalankan melalui penyaduran tanpa elektrik pada substrat kuprum. Kerja penyelidikan dimulakan dengan menghasilkan larutan saduran untuk mencapai sasaran kandungan fosforus saduran, ketebalan dan kekasaran permukaan yang diingini. Untuk menghasilkan saduran ternari *nickel-argentum-phosphorus* (Ni-Ag-P) dan *nickel-copper-phosphorus* (Ni-Cu-P), garam perak dan kuprum telah ditambah ke dalam larutan penyaduran. Saduran ternari terbaik didapati pada saduran yang terkandung 5 mg/L *argentum sulphate* dan 10 mg/L *copper sulphate* yang masing-masing dimendapi oleh 1.14 wt.% Ag dan 3.56 wt.% Cu. Kedua-dua saduran ternari yang dihasilkan mempunyai permukaan lebih rata dan kadar kehausan lebih rendah berbanding saduran binari Ni-P. Peningkatan rintangan haus berkaitan dengan kekerasan lapisan saduran, di mana Ni-Ag-P

mempunyai kekerasan tertinggi (394,08 HK) diikuti oleh Ni-P (380,78 HK) dan Ni-Cu-P (365,34 HK). Walaupun saduran Ni-Cu-P mempunyai kekerasan yang rendah, kekasaran permukaan yang rendah menyumbang kepada kadar kehausan yang rendah. Kekonduksian haba untuk saduran ternari Ni-Ag-P (451.10 W/mK) adalah lebih tinggi daripada saduran Ni-P (445.70 W/mK) dan Ni-Cu-P (326.91 W/mK). Hasilnya adalah seperti yang dijangkakan memandangkan perak mempunyai kekonduksian haba lebih tinggi daripada nikel, dan dengan itu penambahan perak dapat meningkatkan kekonduksian haba saduran Ni-P.

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ABSTRACT

Current functional test of assembled device in semiconductor industry use thermal interface media but it occasionally caused cosmetic defects such as stain or scratch mark. A possible solution to eliminate the undesired defects is by improving the nickel-phosphorus (Ni-P) coating currently applied on the test chuck in terms of the ability to conduct heat transfer efficiently and thus eliminate the use of thermal interface media. Co-deposition of argentum (Ag) and copper (Cu) into Ni-P coating are expected to improve the thermal conductivity of Ni-P coating without sacrificing other coating's properties; surface roughness, thickness, hardness and wear resistance. Ni-P coating in this work was prepared via electroless coating on a copper substrate. The experimental work began by developing the coating solution in order to achieve targeted phosphorus content, thickness and surface roughness. To produce ternary nickel-argentum-phosphorus (Ni-Ag-P) and nickel-copper-phosphorus (Ni-Cu-P) coating, argentum and copper salt were added into the coating solution. The best ternary coating was observed on coating containing 5 mg/L argentum sulphate and 10 mg/L copper sulphate with co-deposition of 1.14 wt.% Ag and 3.56 wt.% Cu respectively. Both ternary coating produced have smoother surface with lower wear rate compared to binary Ni-P coating. Improvement in wear resistance is related to the hardness of coating, in which Ni-Ag-P has highest hardness (394.08 HK) followed by Ni-P (380.78 HK) and Ni-Cu-P (365.34 HK). Even though Ni-Cu-P coating possess low hardness, its low surface roughness contributed to the low wear rate. The thermal

conductivity for ternary Ni-Ag-P coating (451.10 W/m.K) was higher than Ni-P (445.70 W/m.K) and Ni-Cu-P coating (326.91 W/m.K). The result is as expected as argentum has higher conductivity compared to nickel, and thus addition of argentum is able to improve thermal conductivity of Ni-P coating.

CHAPTER 1

INTRODUCTION

1.1 Background

Coating is a layer of material that is applied onto the surface of substrate to provide decorative appearance or functional purpose. Product labels and advertisements are examples of decorative coatings. Functional coatings may be applied to protect the substrate against wear or corrosion while maintaining the substrate material mechanical properties (Palaniappa & Seshadri, 2008). Factors affecting the choice of a coating include service environment, life expectancy, substrate material compatibility, component shape and size, and cost.

While there are several coating techniques, electroless plating have been one of the favourite due to its special properties; simplicity, uniformity, excellent physical and chemical properties and the ability to coat on various surface. Using electroless plating, metallic layer is deposited onto the surface of a part without applying an external electrical circuit. It is widely used as engineering coatings in mechanical, chemical and electronic industries (Sudagar et al., 2012).

The most common metal deposited in electroless plating is nickel. Although there exists variety of other electroless coating such as electroless copper, silver, platinum, palladium, and gold, electroless nickel (EN) has proved its supremacy for producing coatings with excellent corrosion and wear resistance (Tai-xiang & Hui-huang, 2000). The structure of electroless nickel is responsible for some of its unique properties. Electroless nickel coating is a layer of coating form on substrate when dipped in electroless nickel solution bath. It is mainly consist of nickel and its reducing agent. Electroless nickel-phosphorus (Ni-P) coating is the most used EN applied in industry using sodium hypophosphite as the favourite reducing agent. Ni-P coating have received commercial success due to its low cost, ease of control, and ability to offer good corrosion resistance (Balaraju et al., 2003).

Although electroless nickel coatings give satisfactory performance for several applications, there are demands to enhance their performance to meet the needs of engineering application. Improvement of electroless nickel properties was done either by co-deposition of third element or by incorporating hard or soft particles into the Ni-P matrix to form ternary or composite electroless nickel coating. In ternary coating, the third element was added into the electroless nickel solution in the form of salt solution, to be reduced and deposited together with nickel and its reducing agent. Thus, the alloy coating has finer and homogenous coating compared to composite electroless nickel solution which was added in the form of nano or micro particles. The choice of element or particles depends on the specific property that is desired (Ajibola et al., 2014). The ternary coatings that have been studied include nickel-tungsten-phosphorus (Ni-W-P), nickel-copper-phosphorus (Ni-Cu-P), nickel-stannous-phosphorus (Ni-Sn-P), nickel-zinc-phosphorus (Ni-Zn-P), nickel-molybdenum-phosphorus (Ni-Mo-P), nickel-cobalt-phosphorus (Ni-Co-P), and nickel-ferum-phosphorus (Ni-Fe-P) (Balaraju et al., 2006; Constantin, 2014; Ijeri et al., 2014; Pang et al., 2012; Ranganatha et al., 2010; Toda et al., 2013; Wang et al., 2013; Zou et al., 2010).

However, improvement in previous research on Ni-P coating are more focusing on the thermal stability, wear and corrosion resistance of the coating ignoring the importance for the protective coating to possess high thermal conductivity. Currently in electronic industry, Ni-P coating has been successfully applied to provide necessary protection on parts made of copper which has low wear and corrosion resistance. However, Ni-P coating has lower thermal conductivity than copper and this may reduce thermal efficiency of the parts.

Introduction of argentum and copper into Ni-P matrix appears attractive because both elements have unique properties of high thermal conductivity. In the periodic table, argentum (429 W/m.K) and copper (401 W/m.K) has the highest thermal conductivity value compared to other elements. It is expected that co-deposition of high thermal conductivity element into Ni-P matrix will improve the thermal conductivity of Ni-P coating. However, previous investigations reported on the co-deposition of argentum in Ni-P coating are in the form of composite coating (focusing on wear resistance improvement) and not in ternary coating (Alirezaei et al., 2013; Alirezaei et al., 2012; Ma et al., 2009) while study on ternary Ni-Cu-P was done to improve the coating corrosion resistance (Balaraju et al., 2006; Y. Liu & Zhao, 2004; Valova et al., 2010). No reported study was found on the thermal conductivity of ternary Ni-Ag-P and Ni-Cu-P coating.

1.2 Problem Statement

In electronic industry, Ni-P coating was applied on test chuck; a part of testing hardware used for functional test of assembled device in semiconductor industry. Figure 1.1 illustrates the schematic diagram of assembled device with test chuck. The test chuck which was made of copper was coated with Ni-P coating to protect it against wear and corrosion. Unfortunately Ni-P coating possess low thermal conductivity value, thus the test chuck have lower thermal transfer efficiency even though the copper substrate possess high thermal conductivity. Hence, test chuck was not able to conduct heat transfer efficiently and this affected the accuracy of test temperature requirement in functional test.

To overcome this problem, thermal interface media was used in between the test hardware and devices. Media such as interface fluid and solid polymer Thermal Interface Media (TIM) was used to improve the thermal resistance for effective heat transfer during testing. However, the current thermal interface media occasionally leave stain or scratch mark on the device die surface due to mis-process or defective interface media. If those cosmetic defect devices escaped from production, it caused bad quality devices shipped out to customer.

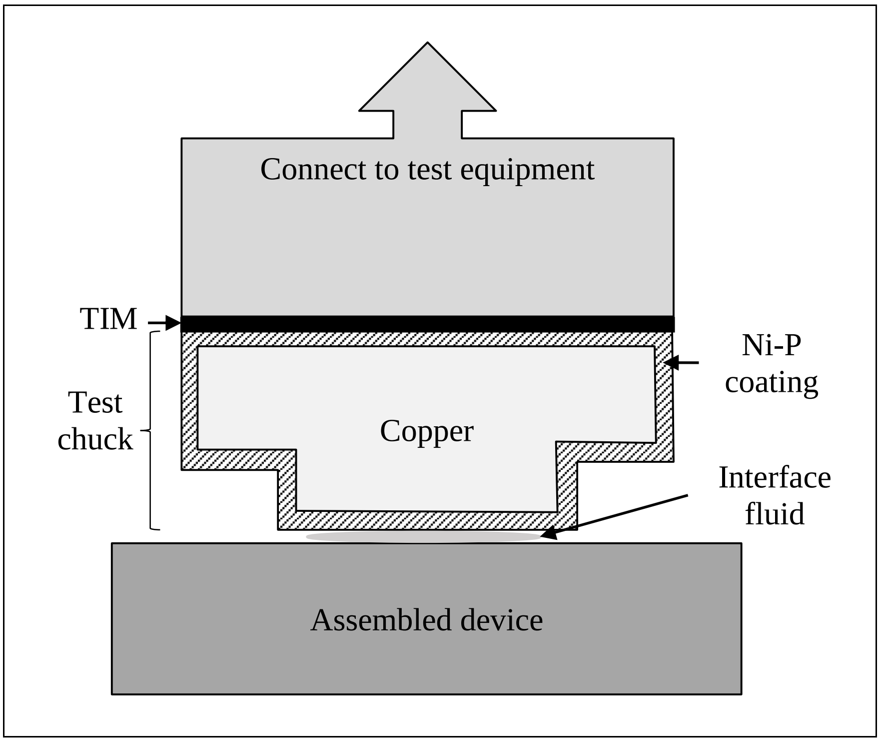

Figure 1.1: Schematic diagram of assembled device with test chuck

To eliminate the undesired devices die surface cosmetic defects, a possible solution is required to eliminate the need of thermal interface media by improving the Ni-P coating currently applied on test chuck. Success of creating much improved Ni coating will eliminate the need of either interface fluid or solid polymer TIM as the Ni-P coating has sufficiently high thermal conductivity and able to conduct heat transfer efficiently. This will improve test process, shorten time required for each test and increase production yield.

Unfortunately, no data was provided by the industry on the test chuck's coating properties or the coating solution. Thus, the current coating on test chuck was characterized and Ni-P coating solution was studied in preliminary study to fabricate coating identical to the coating on test chuck. The coating solution was designed to obtain good coating with high phosphorus content, thickness and smooth surface. The coating was produced on copper sheet to simulate coating on test chuck.

Currently, research on ternary Ni-P coating mostly are focusing on thermal stability, wear and corrosion resistance improvement. However in this project, ternary Ni-Ag-P and Ni-Cu-P coating were studied to improve the thermal conductivity of Ni-P coating. Argentum and copper was selected as they have the highest thermal conductivity value among other elements in periodic table. The coating produced must also show comparable characteristic to the current test chuck, i.e thickness, hardness, surface roughness, and wear rate. This is to ensure that the ternary coating has improved thermal conductivity but maintains the same quality of existing coating on test chuck.