An investigation on FR4 as a based material for Ti/Au and Cu/Au evaporated fabrication for DNA biosensor application

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Abstract. Glass fabricated with Ti/Au is a common technique for DNA in biosensor application. However, the wet etching technique produced poor adhesion for the Ti/Au on the glass. FR4 had been investigated to be used as a based material in this research. Three types of thermal evaporated methods for metal fabrication are investigated; Ti/Au, oxidized Cu/Au, and non-oxidized Cu/Au. In this research, Ti and Cu acts as adhesion layer for Au. A 2 cm length, 1.2 cm width and 1.6 mm thickness of FR4 was used as a base material. The FR4 was cleaned sequentially with acetone and isopropanol then left to dry with nitrogen gas. RF sputtering method is used to deposit Ti whereas copper layer (Cu) remained as it is on the FR4. The Cu/FR4 is cleaned sequentially with acetone and isopropanol and dried with nitrogen. It is found that the adhesion of Ti is good and worked on the FR4 surface. However, a major problem arises when the Ti/Au layer is unsuccessfully removed during the wet etching process. The result shows that non-oxidized Cu/Au fabrication worked well on FR4 as well as during wet etching technique. Hence, it is concluded that FR4 can be used as an alternative based material for Au evaporation in biosensor application. The first section in your paper.

1. Introduction

Silicon, glass and ceramic are common materials used as a base substrate for gold (Au) fabrication by means of immobilization with thiol group at the 5’-end of probe DNAs [1-5]. These substrates are biocompatible and not readily available in the market. Other than that, silicon and glass are hard and brittle, thus difficult for drilling and dicing. It requires complex methodology and equipments such as deep reactive ion etching (DRIE) and diamond-coated cutter for dicing.

Commercialized biosensor screen printed electrode (SPE) i.e; model 220AT produced by DropSens® utilizes different types of metals between sensing electrodes and terminal electrodes. DropSens® utilizes silver at the exposed terminal layer and Au at the sensing electrodes. Material International Anneal Copper Standard (IACS) in Metal Statistics stated that the silver conductivity is 105%, whereas the conductivity of Au is 70%. The Chemical Rubber Company (CRC) Handbook [6] has listed the electrical resistivity for silver and Au to be 15.87 nΩ.m and 22.14 nΩ.m, respectively. The differences in this conductivity and resistivity data proved that there is a possibility on the correlation of the current measurement for different metal fabricated on the same electrode from sensing chamber to the terminal [7].

DNA-based biosensor system incorporates the sensor device and the measurement readout circuitry. Biosensor companies are selling their parts separately. Users have to purchase extra accessories to integrate with the sensor strips. Thus, it will cause an increase in the budget for the...
biosensor system. Moreover, the use of bulky accessories that must be interfaced with the computer limit the portability and in-situ measurement on the biorecognition elements [8]. Therefore, the objective on this research is to evaluate the suitability of non-biocompatible material, Flame Retardant 4 (FR4) for gold (Au) fabrication using thermal evaporator and wet etching techniques throughout all conducting tracks from sensing layer to terminal layer. The used of FR4 as a based substrate in the biosensor development has been demonstrated in this work. None of the published works had reported the application of FR4 in the biosensor fabrication. A standard fabrication of Au throughout the FR4 surface from sensor layer to terminal layer has been implemented by using cost effective technique of thermal evaporation and wet etching.

2. Methodology
A 2 cm length, 1.2 cm width and 1.6 mm thickness of FR4 was used as a base material. The FR4 was cleaned sequentially with acetone and isopropanol then left to dry with nitrogen gas. Two types of thermal evaporated methods for metal fabrication are investigated, Titanium (Ti)/Au fabrication and Copper (Cu)/Au fabrication.

2.1 Ti/Au Fabrication
Radio Frequency (RF) sputtering method is used to deposit Ti and thermal evaporator method is used to deposit Au on FR4. RF power at 210 W, vacuum pressure at 5 X 10^-3 Torr and 2 min exposure produced 30 nm of Ti as an adhesion layer as shown in Figure 1. Then a thermal evaporator of 6.0 x 10^-5 mbar at 68A performed 1 µm Au electrode layer as shown in Figure 2. The Ti and Ti/Au fabricated on FR4-based substrate are shown in Figure 1 and Figure 2, respectively. It is found that the adhesion of Ti is good and worked on the FR4 surface. However, a major problem arises when the Ti/Au layer is unsuccessfully removed during the wet etching process. Previously, a MEMS research had reported the unsuccessful of Ti/Au seed layer by wet etching on the silicon substrate [9 & 10].

![Figure 1. Sputtered Ti on FR4-based substrate.](image1)

![Figure 2. Evaporated Au on Ti/FR4-based substrate.](image2)

2.2 Cu/Au Fabrication with Oxide Layer
A copper layer (Cu) remained as it is on the FR4. The Cu/FR4 is cleaned sequentially with acetone and isopropanol and dried with nitrogen. Au of 0.3g is evaporated directly to this Cu/FR4 using a thermal evaporator of 6.0 x 10^-5 mbar pressure at 68A and performed 1 µm Au electrode layer.

2.3 Cu/Au Fabrication without Oxide Layer
Several researchers had reported a method of copper oxide removal using acetic acid and this method has been implemented in this work [11 - 13]. Original native Cu on FR4 has been immersed in acetic acid at 35°C for 5 to 10 minutes until a shiny copper surface without streaking or hazy residue was observed. Upon removal, the samples were rinsed with DI water and subsequently dried with nitrogen. However, the formation of black residue was observed. Chavez & Hess (2001) reported that the Cu residue was caused by the formation of cupric hydroxide during DI water rinsing step which formed the structure of OH-[11]. However, the acetic
acid treatment without the DI water rinse caused the resulted Cu surface free from oxide formation. DI water rinse is not required since nitrogen drying produces a streak-free and shiny surface [11].

Au of 0.3g is evaporated directly to this Cu/FR4 using a thermal evaporator of 6.0 x 10^{-5} mbar pressure at 68A and performed 1 µm Au electrode layer. Further investigation under SEM image analysis proved that the above mentioned method is effective to remove Cu oxide layer. Figure 3 reflects the SEM image of 900 magnification for the Au deposited on the Cu which was free from oxide layer.

![Figure 3](image)

**Figure 3.** SEM image on the quality of Au deposited on Cu which was free from oxide layer.

3. Results and Discussion

3.1 Ti/Au Fabrication

Figure 4 describes the behaviour during the wet etching of Ti/Au layer on the FR4 substrate. It is noticed that some parts of Ti and Au layer is removed due to the longer time taken for wet etching. It is also found that there is no continuity along the tracks.

Todeschini et al., 2017 in his research found that if mechanical stability is needed for adhesion layers then Chromium (Cr) is suggested [14]. This is due to Cr/Au alloy formation implies a superior electrical and physical contact. The research suggested a thin Cr layer of less than 2 nm as an adhesion layer for mechanical stability and Ti must be avoided. This is due to partially oxidized Ti might form a barrier between the material and the Au overlayer with a consequent deterioration of the electron transport performances.

![Figure 4](image)

**Figure 4.** Weak removal of Ti/Au layer on FR4 substrate.
Radisavljevic et al, 2011 in his research had also reported the unsuccessful contact of Ti/Au for MoS\(_2\) FETs. Interestingly, pure Au outperformed Ti/Au contacts as an adhesion layer [15].

### 3.2 Cu/Au Fabrication with Oxide Layer

The Cu/Au fabrication with oxide layer shows a weak adhesion. It is found that the Au layer can be easily removed even before the soft photolithography process. This phenomenon is shown in Figure 5. Further investigation by SEM image of 1000 magnification found that the oxide layer is formed between the Au and Cu layer as shown in Figure 6. It is believed that the formation of oxide layer caused the poor quality of Au layer adhesion that deposited on the Cu layer. This oxide layer mainly consists of carbon (C) and oxide (O).

![Figure 5. Poor adhesion quality of Au layer on the Cu layer fabricated on the FR4-based.](image1)

![Figure 6. SEM photo on the Cu, Oxide and Au thickness fabricated on the FR4-based.](image2)

### 3.3 Cu/Au Fabrication without Oxide Layer

A major problem on the poor adhesion of Au on the Cu layer is caused by the formation of oxide layer. It is known that Cu is easily oxidized in the open air environment [16]. The oxide layer is removed in order to produce a good and complete adhesion of Au on the Cu. Figure 7 reflects the SEM image of 900 magnification for the Au deposited on the Cu which was free from oxide layer. Figure 8 shows a final biosensor after wet etching and patterning process.
Figure 7. SEM image on the quality of Au deposited on Cu which was free from oxide layer.

Figure 8. A complete fabricated sensor for the area size of 1.04 mm².

4. Conclusion
Three types of thermal evaporated methods for metal fabrication are investigated; Ti/Au, oxidized Cu/Au, and non-oxidized Cu/Au. All these three types of metal fabrication are investigated via the thermal evaporator and wet etching technique. The results showed that oxide free Cu acts as a good adhesion with Au fabricated on FR4-based. Au stayed on the oxide free Cu even after wet etching technique implemented as shown in Figure 8. Thus, it can be concluded that non-oxidized Cu can be used as an adhesion layer for Au fabrication onto FR4-based.

Acknowledgement
This work is sponsored by the Ministry of Higher Education (MOHE) fund from Fundamental Research Grant Scheme (FRGS) with reference no FRGS/1/2018/TK0 4/UiTM/02/35. The financial support is gratefully appreciated.

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