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EFFECT OF ETCHING AS PRE-TREATMENT FOR ELECTROLESS COPPER PLATING ON SILICON WAFER

Shazatul Akmaliah Mior Shahidin[a], Nor Akmal Fadil[a]*, Mohd Zamri Yusop[a], Mohd Nasir Tamin[a], Saliza Azlina Osman[b]

[a]Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
[b]Faculty of Mechanical and Manufacturing Engineering, Universiti Tun Hussien Onn, Johor, Malaysia

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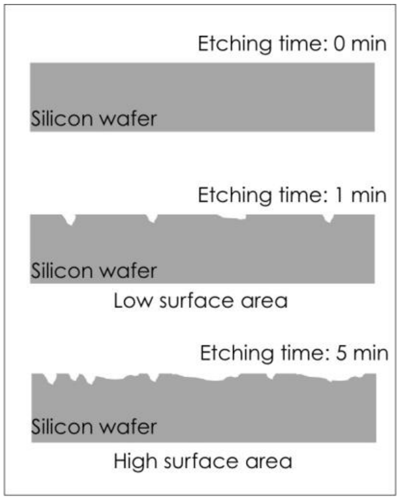
*Corresponding author
norakmal@utm.my

Graphical abstract



Abstract

Metallic coatings, such as copper films can be easily deposited on semiconductor materials like silicon wafer without prior surface pre-treatment using the electroless process. However, the adhesion of the copper film can be very weak and can easily peels off. In this study, the effect of etching in hydrofluoric acid solution as a surface pre-treatment prior to electroless plating on silicon wafer was studied. The etching time in hydrofluoric acid was varied at 1, 3 and 5 minutes in order to investigate the adhesion behaviour of the coating layer. The surface morphology of the electroless plated samples was observed using a field emission scanning electron microscope (FESEM) and the coating thickness was measured using cross sectional analysis. The results showed that longer etching time (5 minutes) produced thicker Cu deposits (8.5µm) than 1 minute etching time (5µm). In addition, by increasing the etching time, the mechanical bonding between the copper film and the substrate is improved.

Keywords: Electroless plating, copper-interconnection, surface pre-treatment, hydrofluoric acid etching, through silicon via (TSV)

Abstrak

Salutan logam seperti filem kuprum boleh disadur dengan mudah ke atas bahan semikonduktor seperti wafer silikon tanpa pra-rawatan permukaan, menggunakan proses penyaduran tanpa elektrik. Walau bagaimanapun, lekatan filem kuprum amat lemah dan mudah tanggal. Dalam kajian ini, kesan punaran dalam larutan asid hidrofluorik sebagai pra-rawatan permukaan sebelum penyaduran tanpa elektrik pada wafer silikon dikaji. Tempoh punaran dalam asid hidroflorik ditetapkan pada 1, 3 dan 5 minit untuk mengkaji tingkah laku lekatan lapisan salutan. Morfologi permukaan sampel saduran tanpa elektrik diamati melalui mikroskop elektron imbasan pancaran medan (*field emission scanning electron microscope*, FESEM) dan ketebalan lapisan saduran diukur melalui analisis keratan rentas. Hasil kajian menunjukkan bahawa tempoh punaran yang lebih panjang (5 minit) menghasilkan lapisan Cu yang lebih tebal (8.5µm) berbanding 1 minit masa punaran (5µm). Tambahan lagi, dengan meningkatkan masa punaran, ikatan mekanikal antara filem kuprum dan substrat bertambah baik.

Kata kunci: Penyaduran tanpa elektrik, interkoneksi kuprum, pra-rawatan permukaan, punaran asid hidroflorik, lubang silikon tembus (TSV)

1.0 INTRODUCTION

Fundamentally, electroless deposition is the reduction of metallic ions from the solution onto the substrate to be metallised without the application of electric current. It is widely used in the fabrication of printed circuit boards due to its low cost, easy deposition and simple process setup [1-5].

Recently, researchers have shown increased interests in electroless copper plating and numerous studies have been conducted to expand the knowledge in this area. These studies have observed that temperature, pH, type of reducing agent, and copper concentration are among the major factors that control the stability of the copper plating bath [6-9]. Electroless copper properties, such as electrical resistivity, crystal orientation, stress and strain measurements, as well as surface roughness have been widely investigated [10, 11]. Furthermore, the mechanisms of electroless copper plating on silicon wafer have also been extensively analysed for better understanding [12-14].

Good adhesion between copper and silicon substrate is of primary concern in relation to physical or chemical surface modifications. Therefore, the pre-treatment process prior to plating is very important to generate nucleation sites for the deposition of copper atoms. In previous studies, Chou et al. [15] and Inoue et al. [16] have considered pre-treatment by using a barrier layer to serve as an effective diffusion barrier to obstruct copper atom from penetrating into the silicon during the electroless plating process. Another study [17] has been conducted on the catalytst perfomance for sensitisation and activation process during pre-treatment, but the study was dedicated for ceramic subsrate only. Nonetheless, there is a lack of studies focusing on the pre-treatment process for the electroless copper deposition on silicon wafer substrate. This paper attempts to investigate the effect of etching using hydrofluoric acid (HF) solution as the pre-treatment process prior to electroless copper plating. The surface morphology, cross sectional analysis and the copper film's thickness were studied.

2.0 METHODOLOGY

A commercially available single crystalline silicon wafer with (100) orientation coated with a thin layer of SiO_2 (thickness: 300 nm) was used as purchased. The wafer was cut into smaller pieces (approximately 1 x 1 cm^2) and was used as a substrate for copper electroless deposition. Figure 1 illustrates the schematic diagram of the electroless copper plating process on silicon wafer. Prior to acid etching treatment, the silicon samples were sonicated in an alkaline cleaning solution for 10 minutes to remove any debris and possible contaminants, as shown in Figure 1b. The surface acid etching effect was studied by etching the samples in 25% volume of hydrofluoric acid solution (49% concentration) in distilled water with various etching times (Figure 1c). Afterwards, the substrate was sensitised by immersing the samples in a sensitisation solution (8 g $SnCl_2$ + 0.6 mL HCl + 200 mL distilled water) for 2 minutes (Figure 1d). This step was followed by surface activation in a solution of 0.03 g $PdCl_2$ + 0.6 mL HCl + 200 mL distilled water for 1 minute at approximately 24°C (room temperature), as shown in Figure 1e. The samples were rinsed with distilled water after each process.

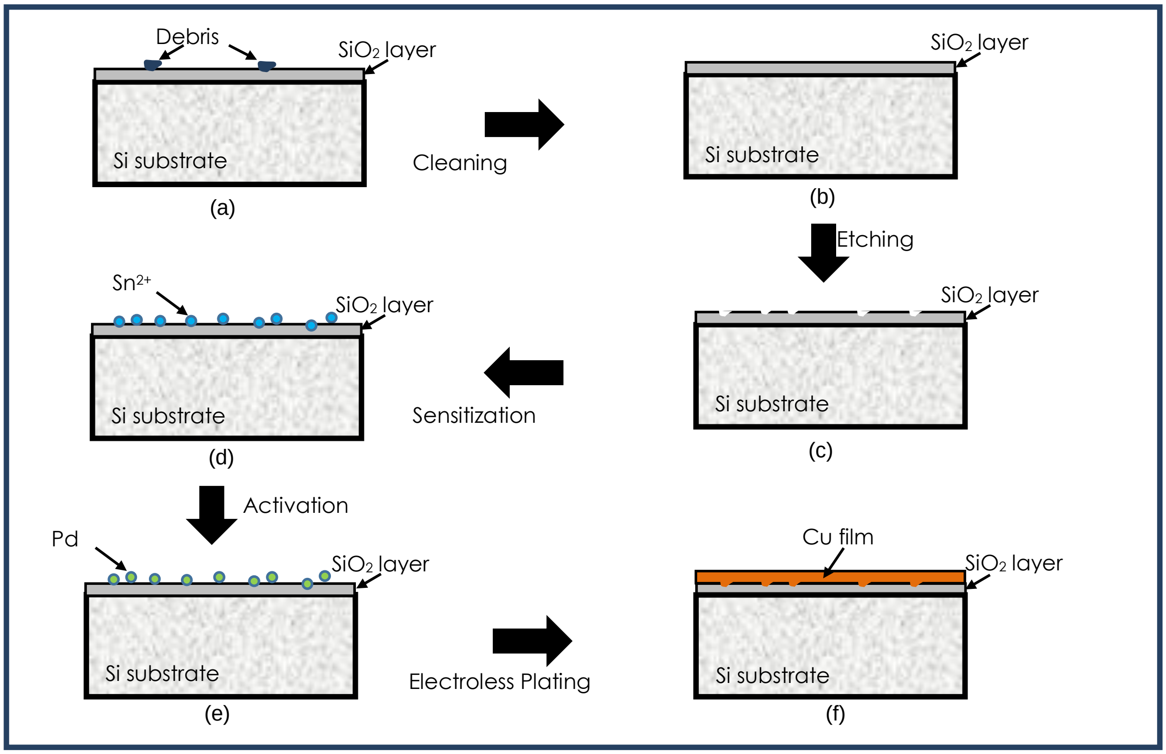


Figure 1 Schematic diagram illustrating the process of electroless plating

The electroless copper plating process on silicon wafer was performed in a 250 mL plating bath a constant pH and temperature. The plating bath consisted of 1.25 g $CuSO_4$ as a metal precursor, 7.5 g EDTA as a complexing agent, 3.75 mL formaldehyde as a reducing agent, NaOH as a pH adjustment agent and 250 mL of distilled water. The pH value of the solution was 12.0, while the temperature was maintained at 70 °C. The plating process was conducted for 10 minutes. The samples were then rinsed with distilled water and left to dry at room temperature.

The morphology of the surface was observed using a field emission scanning electron microscope (FESEM) (Supra 35-VP, Carl Zeiss, Germany) and the thickness of the copper films was measured using the cross sectional analysis feature of the FESEM. The chemical composition of the copper plated samples was measured by using an energy dispersive X-ray spectrometer (EDS) that was equipped on the FESEM.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology of Electroless Copper Plating

Figure 2 shows the surface morphology of the electroless copper deposited samples at different etching times. The results showed that the copper films were uniformly coated on the silicon substrate. The copper films have demonstrated granular morphologies with notable thickness variations. These results were expected since the presence of nuclei promotes heterogeneous island growths that will eventually coalesce into a solid film. Based on the SEM images, it was interesting to note that the agglomeration of copper was found deposited on the copper surface of the etched samples at 3 and 5 minutes (Figure 2b and Figure 2c).

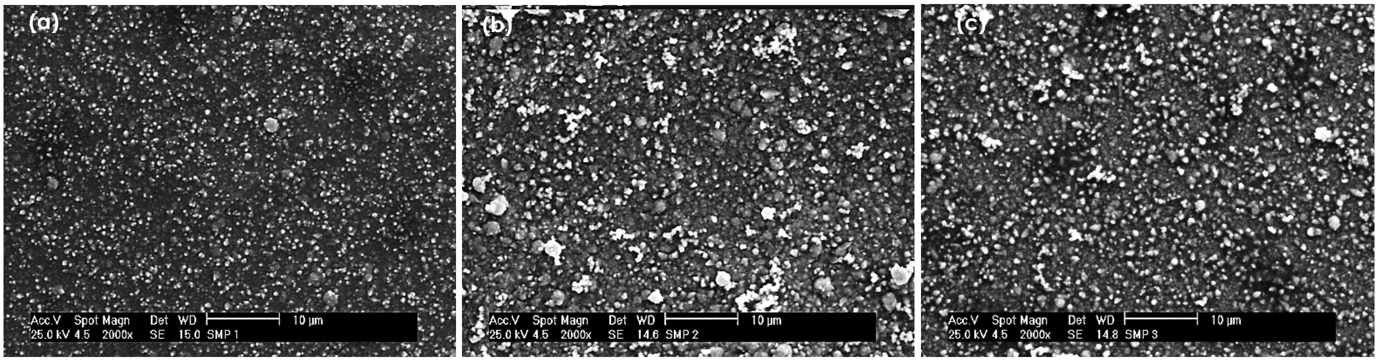


Figure 2 SEM images of electroless copper plated samples, with various etching times; (a) without etching, (b) etching for 3 minutes, and (c) etching for 5 minutes

3.2 Morphology of the Cross Section

Figure 3 shows the FESEM images of silicon substrate surface after the etching process (prior to sensitisation and activation processes) at different etching times. The qualitative analysis of surface morphology by FESEM observation for the as-etched silicon substrate showed no significant differences between 1 minute-etched (Figure 3b) and non-etched sample (Figure 3a). However, 5 minutes-etched sample (Figure 3c) showed clear rougher surface as compared to non-etched sample (Figure 3a).

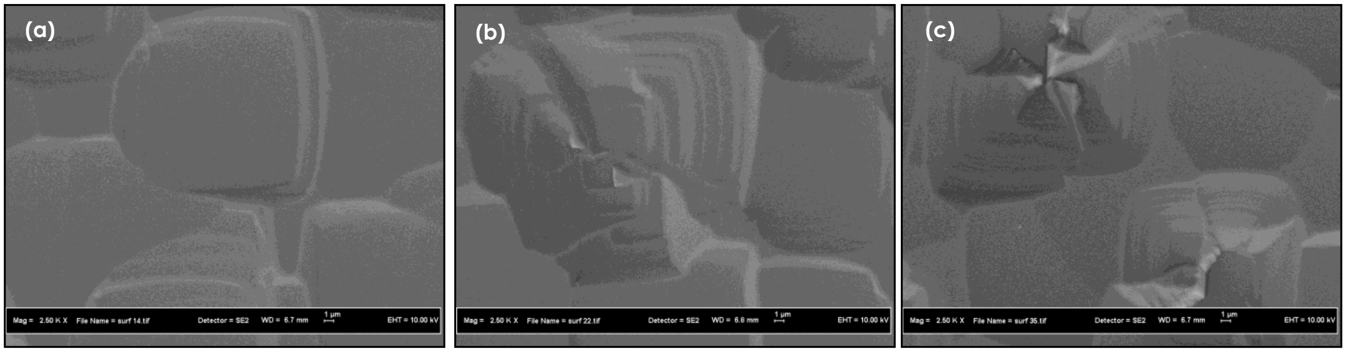


Figure 3 FESEM images of the silicon substrates directly after the etching process, at different etching times; (a) without etching, (b) etching for 1 minute, and (c) etching for 5 minutes

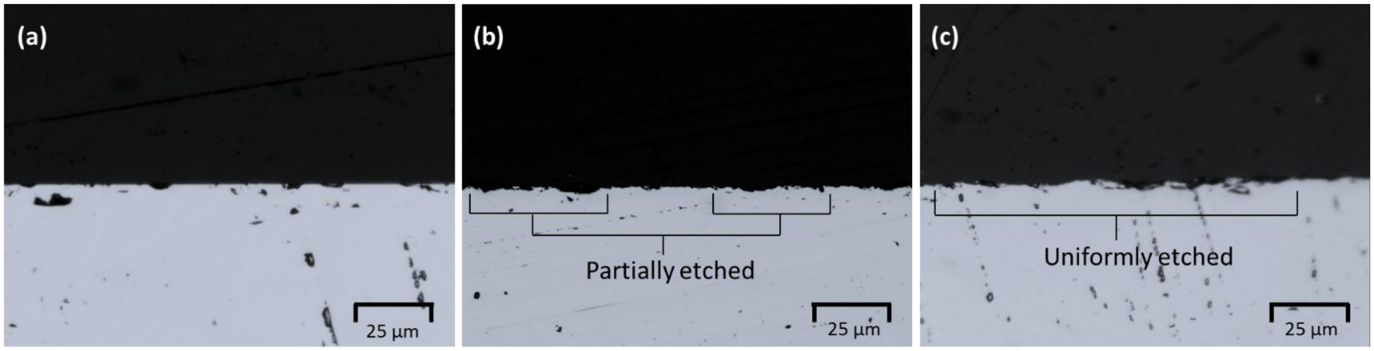


Figure 4 Cross sections of the silicon substrates directly after the etching process, at different etching times; (a) without etching, (b) etching for 1 minute, and (c) etching for 5 minutes

Figure 4 shows the cross sectional images of silicon substrate surface after the etching process. The silicon surface was observed to be partially etched with 1 minute of etching time, as shown in Figure 4b. Meanwhile with 5 minutes of etching time, the silicon surface became rougher and uniformly etched (Figure 4c) compared to non-etched and 1 minute-etched sample. This result shows that the increase of etching time will increase the surface roughness of silicon substrate and thus promote higher hydrophilicity of the surface area. As reported by Ming et al. [18], when the concentration of the hydrofluoric acid solution was increased, the corrosiveness of the hydrofluoric acid solution on the silicon substrate also increased, which resulting in the increment of surface roughness of the silicon surface. This result is in accordance with our present results, where we have investigated the effect of hydrofluoric acid etching time. Without the etching process, the hydrophilicity of the silicon substrate is very weak. The hydrophilicity of the silicon substrate has increased with 5 minutes of etching time.

The performance of copper deposition is greatly influence by adhesion between the copper deposition and the substrate [19]. Electroless plating process is based on the chemical reactions that occur in the water-based plating solution. Therefore, the quality of the deposited metal depends on the hydrophilicity of the solution and the surface to be deposited. Figure 5 shows the FESEM images of the cross sectional samples of the electroless copper plated silicon substrates. Without the pre-treatment process, the adhesion of the copper film on the silicon substrate was very poor, as shown in Figure 5a. It can be seen that the continuous copper film was detached from the silicon surface. In Figure 5b, the adhesion between the copper film and the silicon substrate was much better compared to the sample without the pre-treatment process (Figure 5a). However, a crack-like non-bonded area (marked in Figure 5b) can still be observed between the copper film and the silicon surface, which proved that the adhesion was weak. With the etching time of 5 minutes, the bond between the copper film and the silicon substrate has improved compared to the bonds created without etching and at 1 minute etching time.

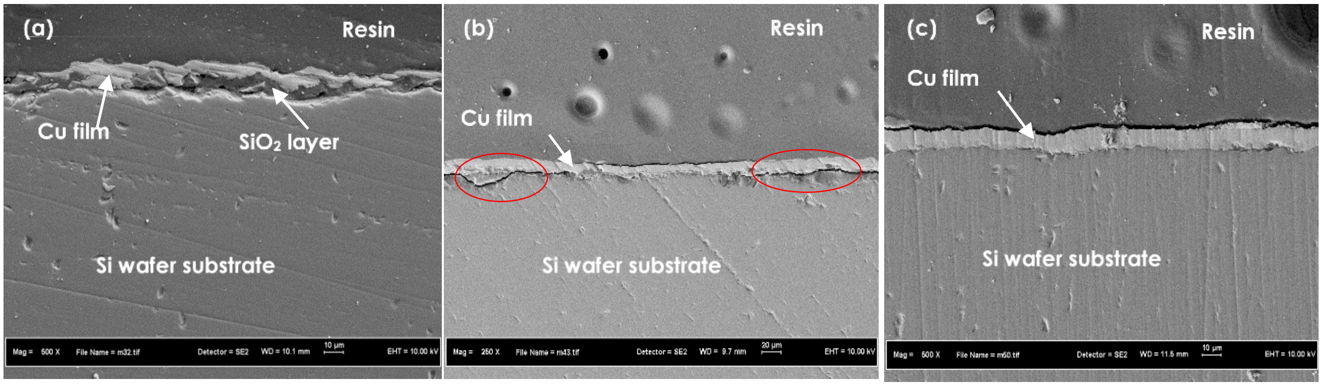


Figure 5 Cross sections of electroless copper plated samples, at different etching times; (a) without etching, (b) etching for 1 minute, and (c) etching for 5 minutes

Figure 6 shows the schematic diagram of growth mechanism for 1 minute-etched and 5 minutes-etched samples starting from sensitising process, activation process and electroless deposition process. 5 minute-etched sample has higher surface roughness compared to 1 minute-etched sample (Figure 6a). In the stage of sensitisation process, silicon wafer which is a non-conductive substrate absorbed the Sn^{2+} ions from the stannous solution. 1 minute etched sample has poor wettability between silicon substrate and sensitisation solution and thus limits the absorbent of Sn^{2+} ions. As 5 minute-etched sample has higher surface roughness and better hydrophilicity, more Sn^{2+} ions from the stannous solution has been absorbed at silicon surface compared to 1 minute-etched sample, as shown in Figure 6b.

Meanwhile in the stage of activation, nucleation effect is performed on the sensitised substrate in the acid palladium chloride solution. Sn^{2+} on substrate surface is eliminated since it reacts with Pd^{2+} in the activation solution. Palladium ions was reduced and deposited on substrate surface to form a Pd cluster. For 5 minutes-etced sample, longer etching time has produced higer surface area as compared to 1 minute-etched sample. The higher the surface area, the greater Pd cluster will deposited (Figure 6c). Greater number of Pd clusters formed has created more nucleation sites on the substrate surface as Pd clusters acted as catalyts for the electroless plating process.

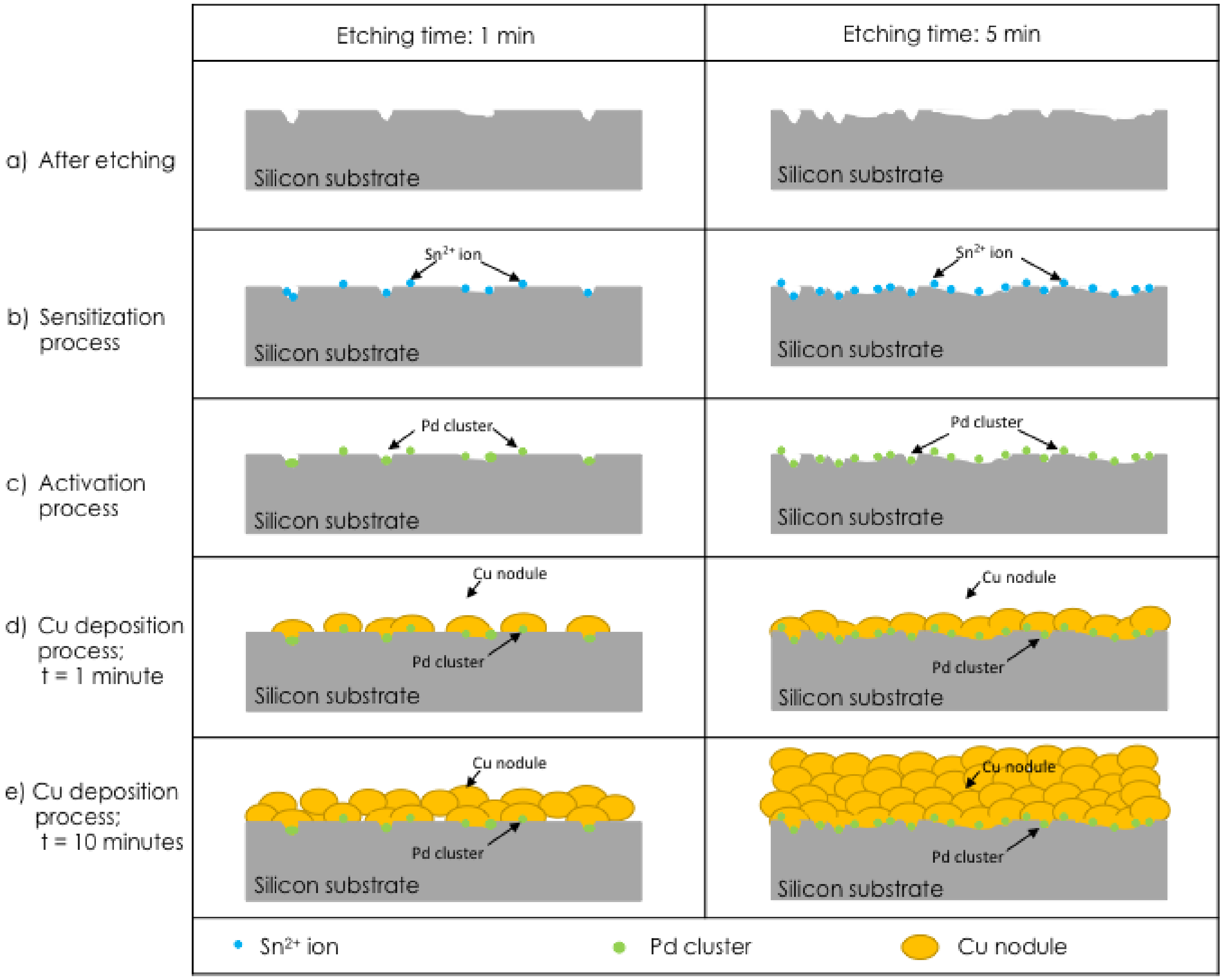


Figure 6 Schematic diagram of growth mechanism of overall electroless copper plating process

For electroless Cu deposition process, autocatalytic reaction between the copper ions and reducing agent in the copper plating will produce metallic Cu atoms (Cu^0) in which Cu^0 will automatically deposited on the activated surface by Pd clusters to form Cu nodules. At 1 minute of electroless Cu deposition time, less Cu nodules formed for 1 minuted-etched sample as compared to 5 minutes-etched sample (Figure 6d). This is due to less nucleation site provided by 1 minute-etched surface thus resulting in slow deposition rate of electroless Cu. 5 minutes-etched samples however produced greater number of Cu nodules at 1 minute of deposition time due to greater number of nucleation sites produced and higher deposition rate occurred at the activated surface. As a result, at 10 minutes deposition time, thicker Cu deposits has produced on the 5 minutes-etched sample as compared to 1 minute-etched sample (Figure 6e). For 5 minutes of etching time, more nucleation sites are helpful to prevent the overgrowth of copper nodules during electroless plating, which will reduce the roughness of the film and increased the quality of the coatings. These factors explain the decreased surface roughness of the copper plated surface at longer etching time, as shown in Figure 5c. In conclusion, the high surface roughness of a substrate will lead to high hydrophilicity, thus resulting in high wettability of the plating solution on the substrate.

The main purposes of etching process are to remove impurities and to create microcavities on the substrate surface in order to increase the sensitisation and activation, which will result in good ion – ion bonding on the surfaces of the particles [20]. However, fluoride-containing electrolytes (HF) are able to dissolve SiO_2 layer. The SiO_2 layer on the silicon surface must be retained since it is essential for electronic applications. Therefore, an optimum etching time must be achieved in order to increase the surface sensitisation and activation without compromise the SiO_2 layer.

Figure 7 shows the energy dispersive X-ray spectroscopy (EDS) mapping for the cross sectional morphologies of the electroless copper plated samples. The SiO_2 layers can be observed in Figure 7a and Figure 7c. However, the SiO_2 layer was not detected for the sample at 5 minutes of etching time, as shown in Figure 7e.

Further analysis was conducted to measure the chemical composition of Cu deposits and the existence of SiO_2 layer on the 5 minutes-etched sample. The chemical composition analysis was conducted using EDS line analysis as shown in Figure 8. Cu deposits was detected at the top surface of substrate (Figure 8c). SiO_2 layer also was detected between the copper films and the silicon substrate at different points of the same sample, as shown in Figure 8.

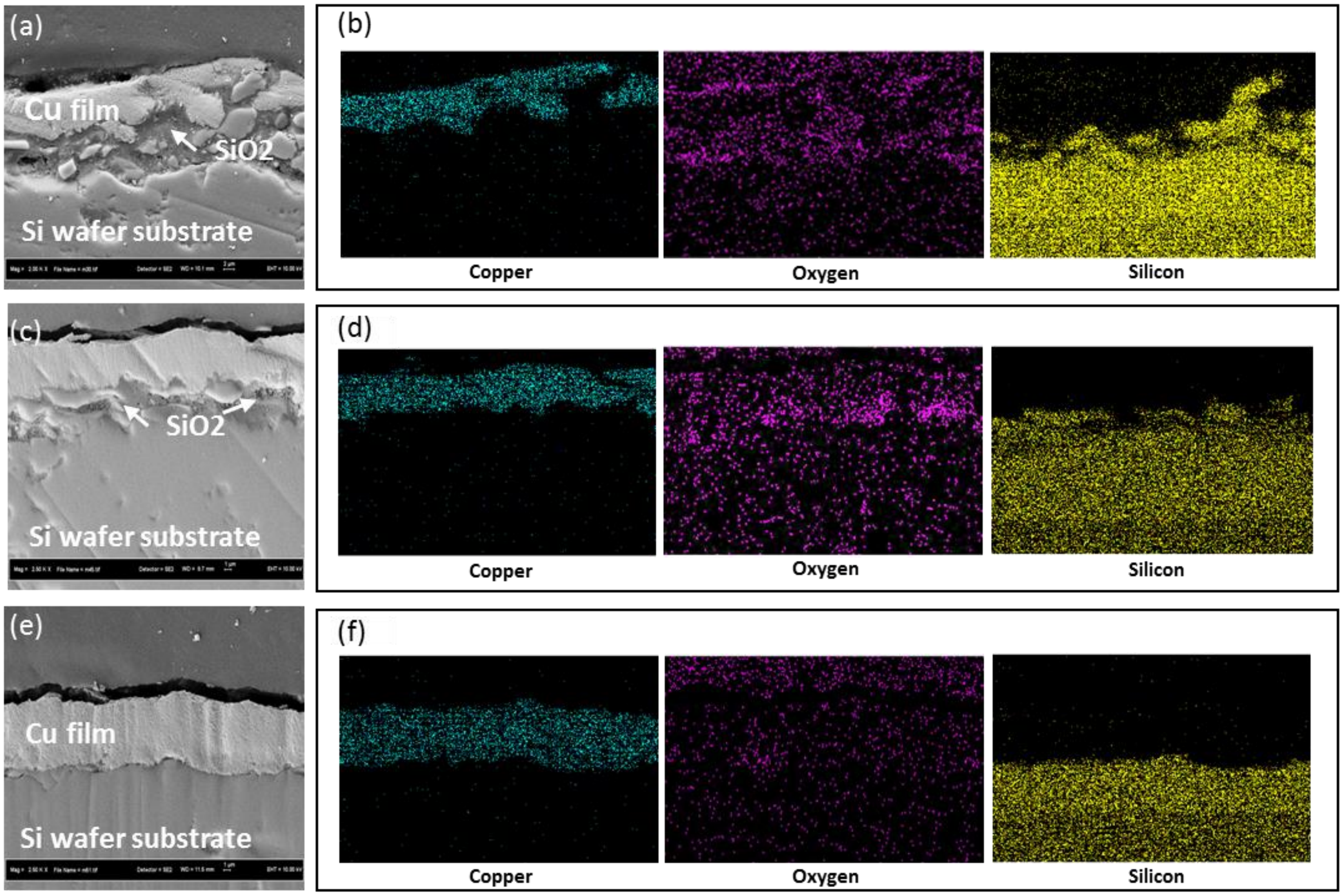
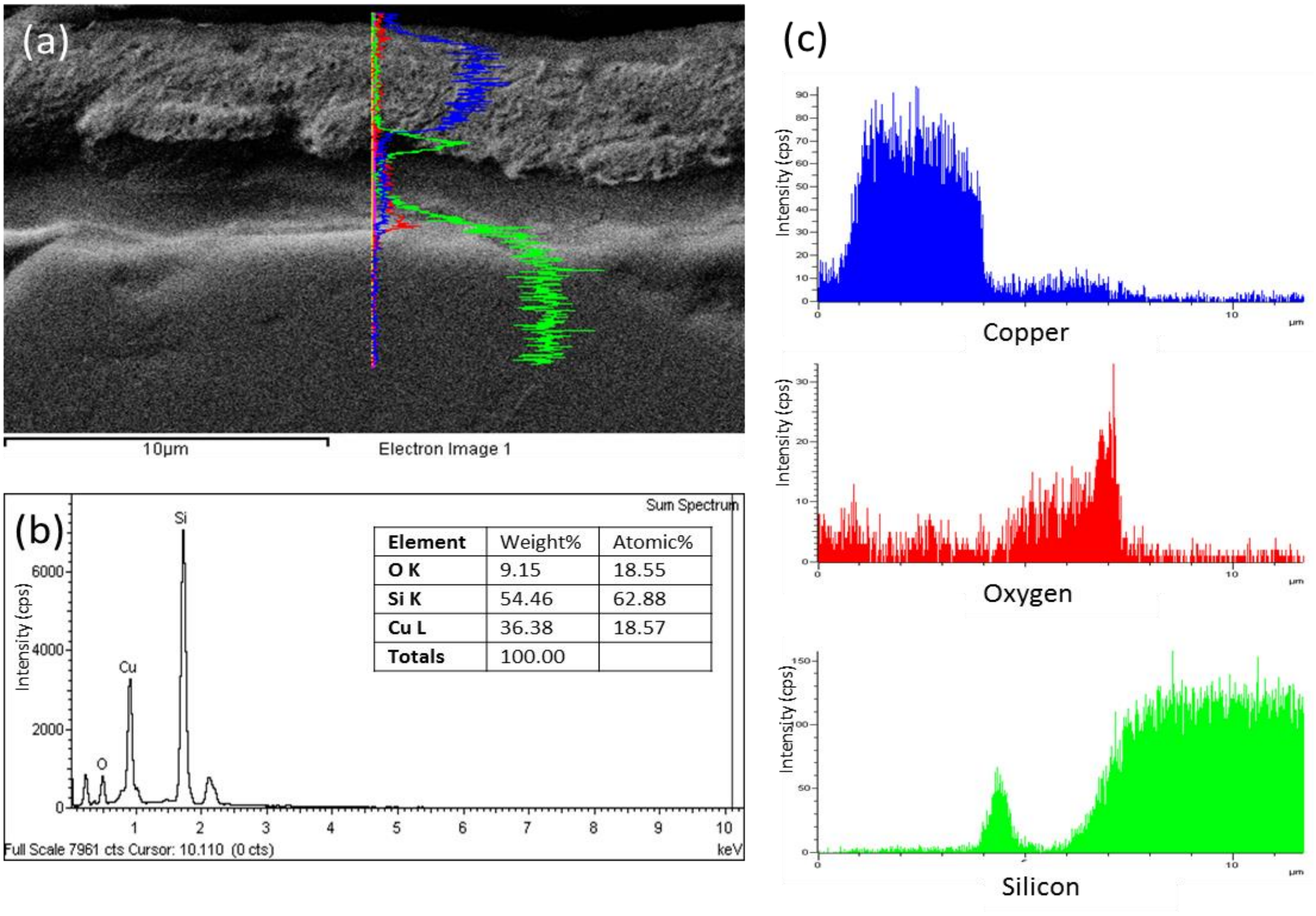


Figure 7 EDS mapping for the cross sectional morphologies of electroless copper plated samples at different etching times; (a) without etching, (b) the EDS mapping for Figure 7a; (c) etching for 1 minute, (d) the EDS mapping for Figure 7c; (e) etching for 5 minutes, and (f) the EDS mapping for Figure 7e



Element	Weight%	Atomic%
O K	9.15	18.55
Si K	54.46	62.88
Cu L	36.38	18.57
Totals	100.00	

Figure 8 Energy dispersive X-ray spectroscopy (EDS) line scanning for the cross sectional morphology of 5 minutes-etched electroless copper plated sample

3.3 Effect of Etching towards Copper Film Thickness

Figure 9 shows the average thickness of the copper films deposited on the silicon samples at different etching time. As discussed in section 3.2, deposition rate is increased with the increase of etching time. Based on Figure 9, it is apparent that the thickness of the copper films deposited on the silicon substrates has increased with the increased of etching time. A polynomial relationship between the deposition time and copper film thickness was observed.

4.0 CONCLUSION

Electroless copper plating can be done on the silicon surface with or without the surface treatment process. However, it will affect the bonding at the interface between the copper film and the substrate. The silicon substrate that has been pre-treated via etching for 5 minutes has stronger adhesion as compared to the other etching time. High surface roughness of a substrate will lead to high hydrophilicity, thus resulting in high wettability of the plating solution on the substrate. However, the etching time should be controlled in order to prevent the total removal of the silicon dioxide layer.

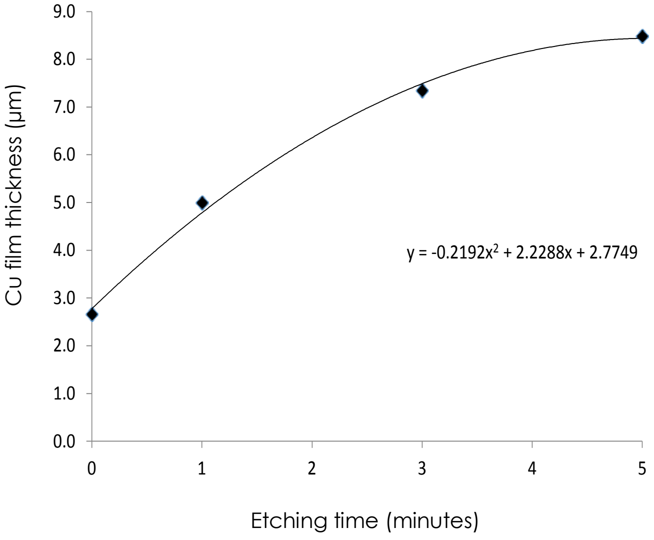


Figure 9 Effect of etching times towards copper film thickness

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References

[1] Niazi, A. R., Li, S., Wang, Y., Liu, J., Hu, Z., and Usman, Z. 2014. Parameters Optimization of Electroless Deposition of Cu on Cr-Coated Diamond. *Trans. Nonferrous Met. Soc. China*. 24: 136-145.

[2] Hantang Qin, Jingyan Dong, and Yuan-Shin Lee. 2017. AC-pulse Modulated Electrohydrodynamic Jet Printing and Electroless Copper Deposition for Conductive Microscale Patterning on Flexible Insulating Substrates. *Robotics and Computer-Integrated Manufacturing*. 43: 179-187.

[3] Jianhui Lin, Chong Wang, Shouxu Wang, Yuanming Chen, Wei He, and Dingjun Xiao. 2016. Initiation Electroless Nickel Plating by Atomic Hydrogen for PCB Final Finishing. *Chemical Engineering Journal*. 306: 117-123.

[4] Shacham-Diamand, Y, Dubin, V., and Angyal, M. 1995. Electroless Copper Deposition for ULSI. *Thin Solid Films*. 262: 93-103.

[5] Shacham-Diamand, Y., Lopatin, S. 1999. Integrated Electroless Metallization for ULSI. *Electrochimica Acta*. 44: 3639-3649.

[6] Guazzone, F., Engwall, E. E., Mardilovich, I. P., and Ma, Y. H. 2004. Kinetics and Microstructure of Cu Deposits from Electroless Plating Baths. *Am. Chem. Soc., Div. Fuel Chem*. 49(2): 896.

[7] Hanna, F., Hamid, Z. A., and Aal, A. A. 2003. Controlling Factors Affecting the Stability and Rate of Electroless Copper Plating. *Materials Letters*. 58: 104-109.

[8] Anik, T., Touhami, M.E., Himm, K., Schireen, S., Belkhmima, R.A., Abouchane, M., and Cissé, M. 2012. Influence of pH Solution on Electroless Copper Plating using Sodium Hypophosphite as Reducing Agent. *Int. J. Electrochem. Sci*. 7: 2009-2018.

[9] M'hanni N., Galai M., Anik T., Ebn Touhami M., Rifi E.H, Asfari Z., Touir R. 2017. Influence of Additives Selected Calix[4]Arenes on Electroless Copper Plating Using Hypophosphite as Reducing Agent. *Surface and Coatings Technology*. 310: 8-16.

[10] Ee, Y. C., Chen, Z., Chan, L., See, A. K. H., Law, S. B., Tee, K. C., Zeng, K. Y., and Shen, L. 2004. Effect of Processing Parameters on Electroless Cu Seed Layer Properties. *Thin Solid Films*. 462-463: 197-201.

[11] Sharma, T., Bruning, R., Nguyen, T. C. L., Bernhard, T., and Bruning, F. 2015. Properties of Electroless Cu Films Optimized for Horizontal Plating as a Function of Deposit Thickness. *Microelectronic Engineering*. 140: 38-46.

[12] Filho, S. G. d. S., Pasa, A. A., and Hasenack, C. M. 1997. A Mechamism for Electroless Cu Plating onto Si. *Microelectronic Engineering*. 33: 149-155.

[13] Paunovic, M. 2010. Electroless Deposition of Copper. In *Modern Electroplating*. Fifth Edition. M. Schlesinger and M. Paunovic, Eds. New Jersey, USA: John Wiley & Sons, Inc. 433-445.

[14] Sung-Te Chen, Yu-Cheng Chung, Jau-Shiung Fang, Yi-Lung Cheng, and Giin-Shan Chen. 2017. Enhancement of Seeding for Electroless Cu Plating of Metallic Barrier Layers by Using Alkyl Self-Assembled Monolayers. *Applied Surface Science*. 405: 350-358.

[15] Chou, Y. H., Sung, Y., Bai C. Y., and Ger, M. D. 2008. Effects of Molybdate Concentration on the Chracteristics of Ni-Mo-P Diffusion Barriers Grown by Nonisothermal Electroless Deposition. *Journal of the Electrochemical Society*. 155: 551-557.

[16] Inoue, F., Shimizu, T., Yokoyama, T., Miyake, H., Kondo, K., Saito, T., Hayashi, T., Tanaka, S., Terui, T., and Shingubara, S. 2011. Formation of Electroless Barrier and Seed Layers in a High Aspect Ratio through-Si Vias using Au Nanoparticle Catalyst for All-Wet Cu Filling Technology. *Electrochimica Acta*. 56: 6245-6250.

[17] Ma, H., Liu, Z., Wu, L., Wang, Y., and Wang, X. 2011. Study of a Pre-treatment Process for Electroless Copper Plating on Ceramics. *Thin Solid Films*. 519: 7860-7863.

[18] Hu, M., Su, Y. F., and Wu, M. Z. 2009. Influences of Pretreatment Solution Concentrations on Copper-Doped SiC Particles Made through Electroless Plating Technique. *Advanced Materials Research*. 79-82: 1739-1742.

[19] Xu, C., Chen, L., Yu, L., Zhang, J., Zhang, Z., and Wang, J. 2014. Effect of Pickling Processes on the Microstructure and Properties of Electroless Ni-P Coating on Mg-7.5Li-2Zn-1Y Alloy. *Material International*. 24: 655-662.

[20] Levy-Clement, C., Lagoubi, A., Tenne, R., and Neumann–Spallart, M. 1992. Photoelectrochemical Etching of Silicon. *Electrochimica Acta*. 37(5): 877-888.