JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Electroless Cu Deposition on Si Needles with Diffusion Constraints

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Abstract

Silicon needles or micro wires have been produced using galvanostatic electrochemical etching and chemical over etching respectively. A 6 inch p-type (100) silicon wafer with resistivity 15-24 Ω cm and aluminum on the back side was used as starting material. Chemical over etching was performed in two steps: first, a treatment for passivating the surface of Si using an aqueous solution of polyethylene glycol and second, the Si needles were transferred immediately into the etchant which is an aqueous solution containg PEG and potassium hydroxide (KOH) pellets. The effect of varying the deposition parameters for electroless Cu deposition on silicon microwires is the main focus of this work. The bath solutions used for electroless Cu deposition were varied according to bath composition and composition concentration and additives.

1. Introduction

Different deposition techniques have been used for metallization of copper in microelectronic devices. These include vacuum-based deposition, like physical vapor deposition (PVD), chemical vapor deposition (CVD) [1], and electrochemical deposition (electroplating and electroless plating) techniques [2]. However, vacuum-based deposition techniques have drawbacks such as poor step coverage in deep sub-micrometer dimension features, resulting in problems like overhangs or voids [1-6]. According to this, electrochemical Cu deposition is the technique of choice when depositing in cavities and microstructures. Hence this article focuses on the electroless deposition of copper on Si needles with diffusion constraints.

Electroless deposition (ELD) covers quite a range of chemical deposition processes at the solid/liquid interface. ELD is considered as a combination of two electrochemical reactions, the reduction of metal ion to the zero-valent state and the oxidation of the reducing agent. The electrons required by the first reaction must be supplied by the second, resulting in an overall reaction. Electroless Cu deposition is the reduction of copper ions in a solution by a reducing agent [3,13]. There are two main approaches used for electroless Cu deposition: deposition in basic solutions and deposition acidic solutions.

Acidic solution approach for electroless Cu deposition is the focus of this work. The known solution for this approach is HF. The deposition is performed at 30°C within 5 minutes [7]. Copper deposition on silicon from fluoride-containing solutions for metallization of microelectromechanical systems (MEMS) devices is concerned. This method exploits the reducing behavior of elemental silicon toward noble metal ions in aqueous solutions containing fluoride ions. The process can be described by the two half-cell reactions:

$$Si + 6F^{-} \rightarrow SiF_6^{2-} + 4e- \quad (2.6)$$

$$2Cu^{2+} + 4e- \rightarrow 2Cu \quad (2.7)$$

From the above equations it can be seen that Si reacts with HF releasing 4 electrons; these electrons are accepted by Cu^{2+} ions, leading to the direct Cu deposition on the Si surface. This approach has been lately used for the deposition of a Cu seed layer on silicon microwires or needles. The deposition rate, coverage, and depth are determined by the bath solution composition and concentration and additives.

The effect of the additives polyethylene glycol (PEG) on Cu2+ reduction onto Si needles in acidic sulfate solutions has been examined and results diffusion constraints of the Cu2+ reduction at the top of the si-needles. As per the diffusion mechanism from the gradual loss of Cu2+ reduction inhibition with increasing over potential at high PEG sudden and complete breakdown of the inhibiting film at a

critical potential when additives are used. Therefore, by optimizing the amounts of the reactants, the deposition is found on the top of the needles. In Fig. 1 it is shown an array of Si needles with a Cu layer until a stabilizing layer [20].

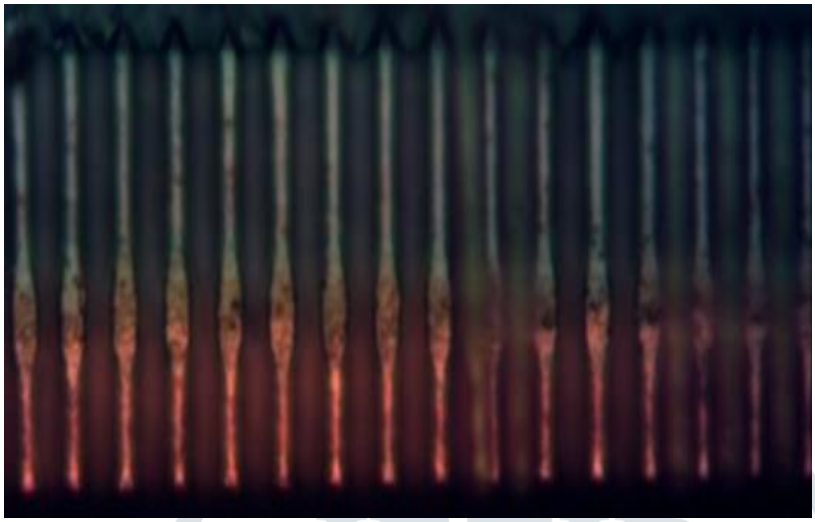


Fig. 1. Electroless deposited Cu seed layer on Si needles.

2. Experimental

The samples used for the electroless Cu deposition were Si needles of 1 µm in diameter, joined together through a stabilizing layer found at 9µm from the top. The total length of the wires is 24 µm.

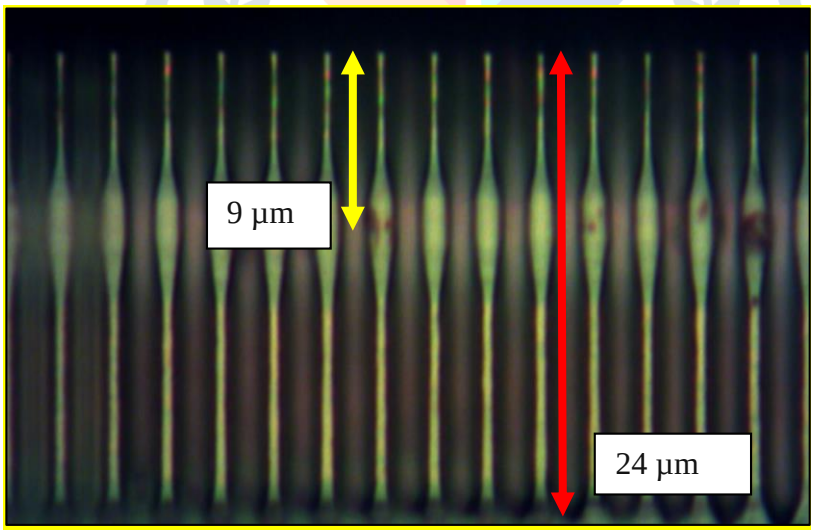


Fig.2. The fabricated Si needles.

The following methods are used for fabrication of the Si needles.

2.1. Patterning of the Si wafers

A 6 inch p-type (100) silicon wafer with resistivity 15-24 Ω cm and aluminum on the back side was used as starting material. A quadratic array of dots was structured on the surface of the wafers by standard photolithography and reactive ion etching [19]. The structured silicon wafer was then treated with KOH solution to create inverted pyramids. The solution was a 20 wt % aqueous solution of KOH with 0.5 g/100 mL of polyethyleneglycol 3400 Sigma – Aldrich. This etching process was done for 45 minutes at 50°C.

2.2. Electrochemical pore etching

Galvanostatic electrochemical etching with the current profile shown in Fig. 3 is used to produce macropores. The etching process was done by a complete etching system from ET & TE. The electrolyte used for the etching was composed of 22 mL HF 48%, 220 mL DMF (N, N-dimethylformamide) and 2 g PEG.

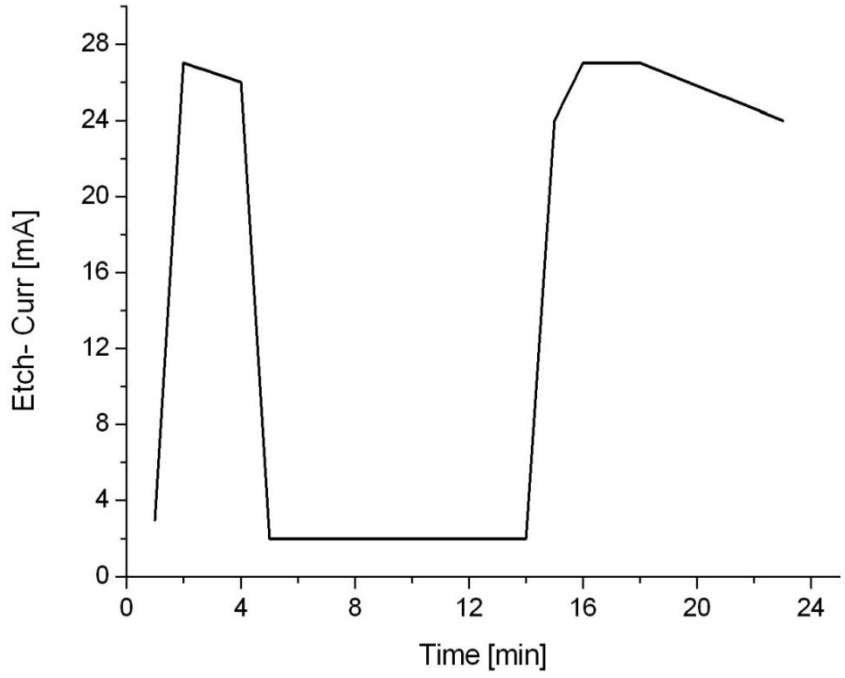


Fig. 3. Current profile used for macropore etching.

2.3. Chemical over etching of macroporous Si to obtain the needles

Chemical over-etching is used to consume the walls of the pores, leaving micro-wires or Si needles staying. This process consists of two steps. First, a treatment for passivating the surface using an aqueous solution of 5 g/Lt of polyethylene glycol 3400 Sigma-Aldrich for 30 min at 50°C was performed.

Chemical over-etching is used to increase the pore diameter of wires. And after passivation the Si needles were transferred immediately into the etchant (100 mL) which is an aqueous solution of 2 g of polyethylene glycol 3400 and 0.45 KOH. The etching was performed for 1h 35 minutes at 50°C.

2.4. Electroless copper deposition

Copper is deposited chemically with a mixture of deionized H_2O, 48% HF and $CuSO_4.5H_2O$ (M = 249.68 g/mol).

Here, the study of the effects of varying the deposition parameters for electroless Cu deposition is the main focus; then the bath solutions used for electroless Cu deposition were varied according to bath composition and composition concentration [15].

Additionally, a couple of additives were tested in different concentrations. Polyethylene glycol (PEG) 3400 Sigma-Aldrich was used as surfactant. On the other hand, ethylenediamineteteraacetic acid (EDTA) Alfa Aesar was used as a chemical complexer.

3. Results and discussion

3.1. Electroless copper deposition

Electroless deposition (ELD) is the process of depositing a coating with the aid of a chemical reducing agent in a solution without the application of external electrical power. In ELD an electron-transfer reaction takes place, where electrons are transferred from a reducing agent to the metal ion [12]. For understanding the deposition mechanisms of Copper on Si needles varied with different parameters or bath solution composition used.

3.1.1. Effect of varying the amount of hydrofluoric acid

For these experiments, 1.9 g of $CuSO_4 \cdot 5H_2O$ and 98 mL of DI H_2O with 1, 2, 3, 4, 5, and 6 ml of 48% HF was studied. All the experiments were done for 5 minutes at 30 °C.

After the deposition, the Si needles were investigated by optical microscope. The copper coverage on the different needles varied according to the amount of hydrofluoric acid used. Among the six chemically copper deposited needles, two of them were selected based on the quality of needles produced. Sample "A" (Fig. 4), obtained using 1 mL of HF, and was selected as the sample with the poorest deposition of copper. And the sample obtained by using 4 mL of HF Sample "B" is the best Cu coverage (see Fig. 5).

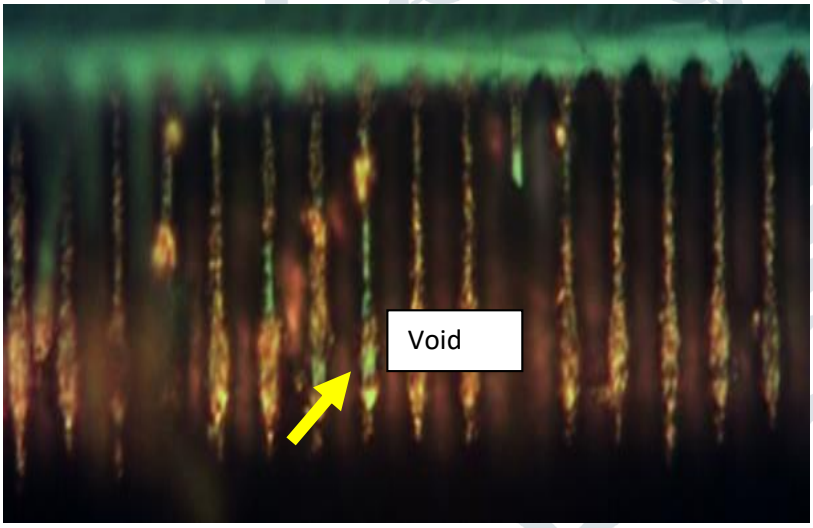


Fig. 4. Copper deposited on Si needles by 1.9 g of $CuSO_4.5H_2O$ and 1 mL of 48% HF.

In sample "A" a large number of defects such as voids and seam is observed. Agglomeration of copper particles is also observed. This affects the current carrying capacity of the films by increasing the resistivity of the film. The poor coverage mainly happens due to the amount of HF was very small to produce the necessary electrons to reduce Cu^{2+} to Cu^0. On the other hand, Cu deposits were found even in the base area of the needles, indicating a slow reaction rate on the top which gives the Cu ions to diffuse into the depth.

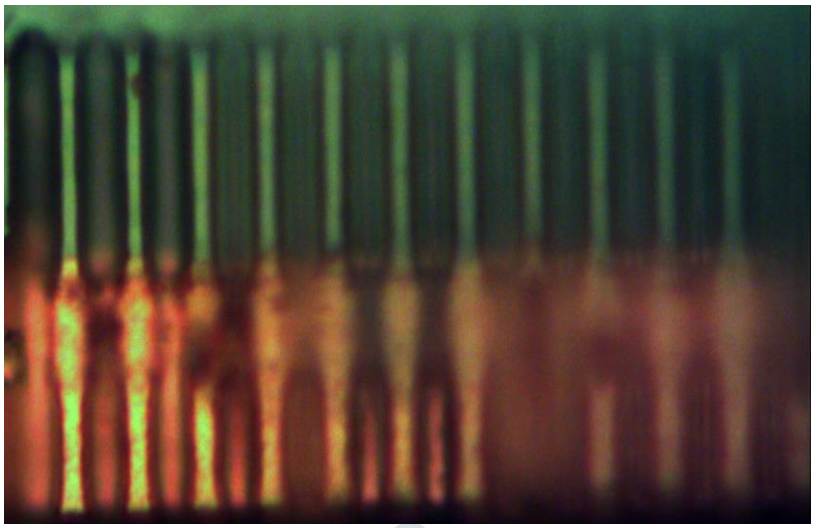
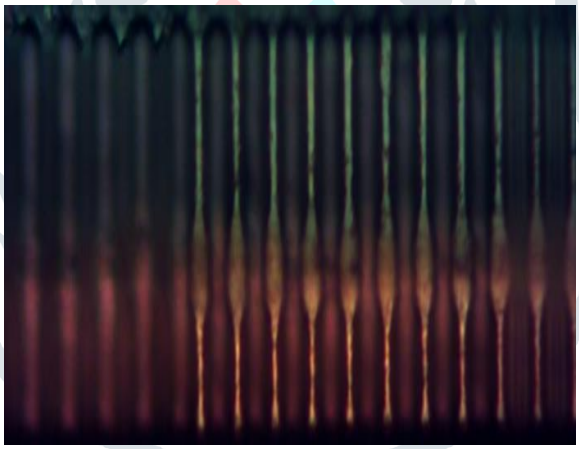


Fig. 5. Copper deposited on Si needles by 1.9 g of $CuSO_4.5H_2O$ and 4 mL of 48% HF.

Deposition of copper up to the support layer is observed in sample "B". In this case the amount of HF was enough to release plenty of electrons which are needed to reduce the copper ions. This makes the deposition more homogenous with a good coverage. The deposition goes just until the support layer because the Cu ions are totally consumed on the top, due to the availability of electrons. As a result of this, the quality of the film is good, but some voids are still present.



3.1.2. Effect of varying amount of $CuSO_4.5H_2O$

In this experiment Cu deposition was performed by varying the amount of $CuSO_4 \cdot 5H_2O$ while keeping the amount of HF and DI H_2O constant. Some samples were prepared using **1 mL HF** and others using **4 mL HF**, following the recipes for the **best** and **worst** sample from **section 3.1.1**. All the depositions were done for 5 minutes at 30°C.

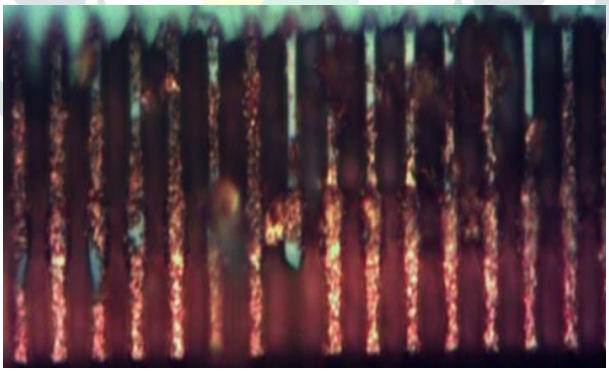
Electroless Cu deposition by using 0.5, 1.9 and 3 g of $CuSO_4.5H_2O$ and 98 mL DI H_2O and 1 mL of 48% HF of the worst sample was examined. The chemically Cu deposited needles were investigated by optical microscope. The copper coverage on the different needles varied according to the amount of $CuSO_4.5H_2O$ used. The chemically Cu deposited needles were compared based on the quality of the needles produced. Among the different needles above, 'Sample A' was selected as best deposition of copper on the support layer, Fig. 6. 'Sample B' shows the poorest deposition of copper on the support layer and was used for subsequent experiments, Fig. 7.

In this case copper was deposited until the support layer. And 1 mL of 48% hydrofluoric acid was enough to reduce Cu^{2+} to Cu^{0}. Hence, a good conducting seed layer of copper was formed.

Fig.6. Cu deposited on Si by 0.5 g of $CuSO_4.5H_2O$ and 1 mL of HF.

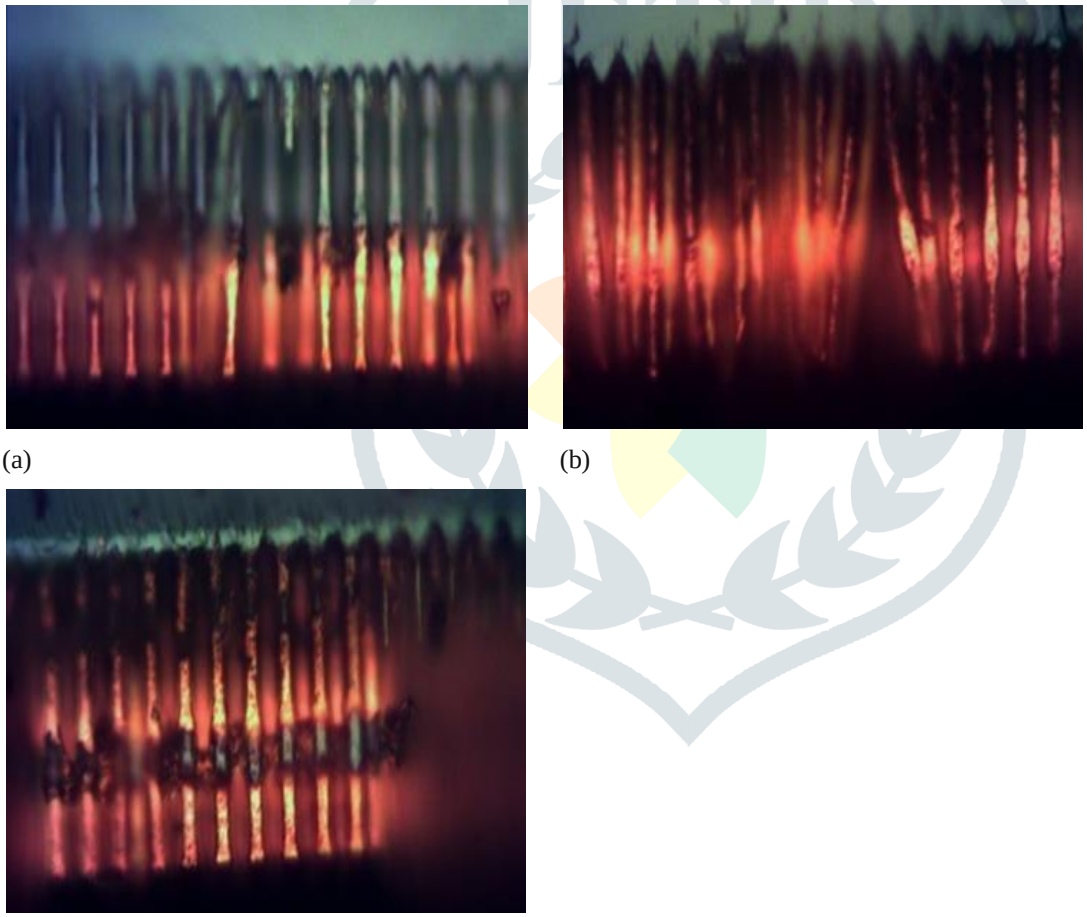
As the amount of $CuSO_4.5H_2O$ increased, poor deposition of copper on the wires was observed. Agglomeration of copper particles, formation of voids, and deposition of copper on the base area of the needles were some phenomenon observed.

Fig. 7. Cu deposited on Si by 3g of CuSO4.5H2O and 1 mL of HF.



Electroless Cu deposition by using 0.5 g, 1.9 g and 3g of $CuSO_4.5H_2O$, 4mL of 48% HF and 98 mL DI H_2O was also examined. The chemically Cu deposited needles obtained by varying the amounts of $CuSO_4.5H_2O$ were investigated by optical microscope. Formation of copper seed layer on the different needles varied according to the amount of $CuSO_4.5H_2O$ used. The chemically Cu deposited wires were compared based on the filling behavior of copper until the support layer which is conductive enough to carry current, as depicted in Fig. 8

As the amount of $CuSO_4.5H_2O$ increases, the quality the Cu deposited on Si needles decreases. And deposition of Cu up to the support layer is observed for 0.5 g of $CuSO_4.5H_2O$ Figure 3.5 (a). Hydrofluoric acid reacts with Si and releases electrons that are required to reduce the $Cu^{2+}$to Cu^0. In comparison to Figure 8 (b), in Fig. 3.5 (a) the filling of copper up to the support layer is successful; this is due to the diffusion limitation of Cu at small amounts. In Fig. 8 (b) copper is deposited on the support layer that contains defects (voids and seams) which affects the current carrying functionality of the needle. In Fig. 8 (c) deposition of copper on the base area of the wires is observed. This is mainly because of the diffusion of cu particles through the needles increased at large amounts. Apart from deposition of Cu on the base area of the needle, formation of voids or (seams) is observed. At large number of voids, there could be a possibility that the electrolytes trapped in and results copper corrosion.



(a) (b)

(c)

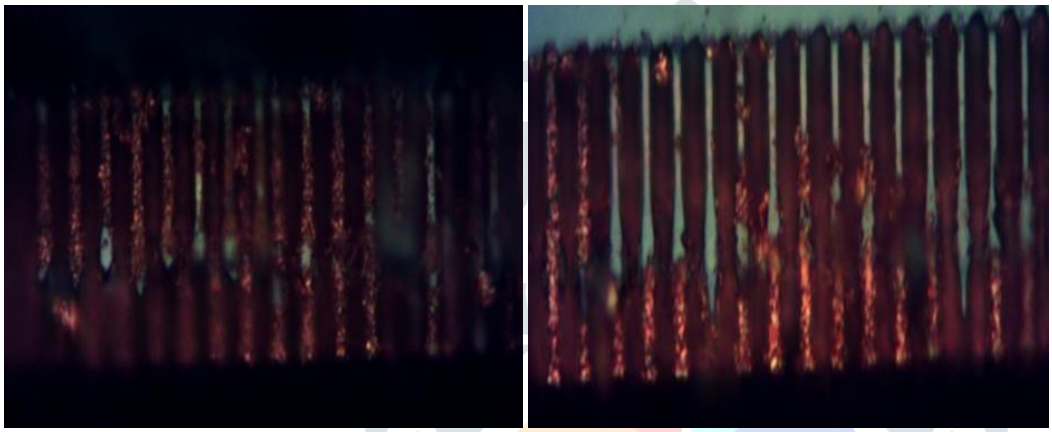
Fig. 8. Cu deposited on Si needles by varying amount of $CuSO_4.5H_2O$ (a), (b), (c); 0.5 g, 1.9g , 3 g of $CuSO_4.5H_2O$ and 4 mL of HF.

3.1.3. Electroless Cu deposition with additives (PEG)

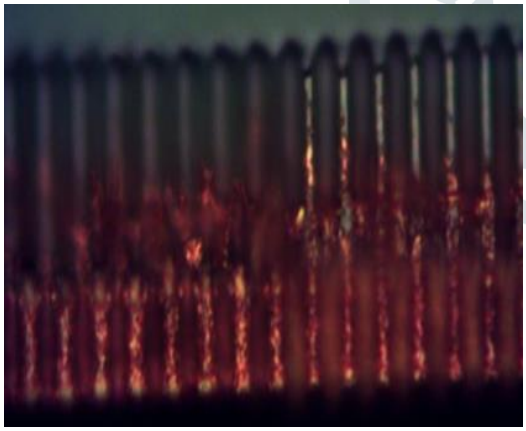
Electroless deposition of copper on different Si needles by different PEG addition was performed for 5 minutes at 40°C. The Cu deposited needles were observed by optical microscope.

Electroless Cu deposition for solution containing 3 g of $CuSO_4.5H_2O$ and 1 mL of HF at different PEG addition (0.5g, 1g and 2g) was examined.

Effect of polyethylene glycol additives on electroless Cu deposition can be described as a formation of passivation layer that prevents diffusion of copper on the desired depth of the needle. In Fig. 9 (a) to Fig. 9 (c) there is no formation of copper seed layer. This is mainly because of PEG inhibits the reduction of copper. So that copper particles are randomly distributed through the needles. The needles produced at different PEG addition are depicted below in Fig. 9.



(a) (b)



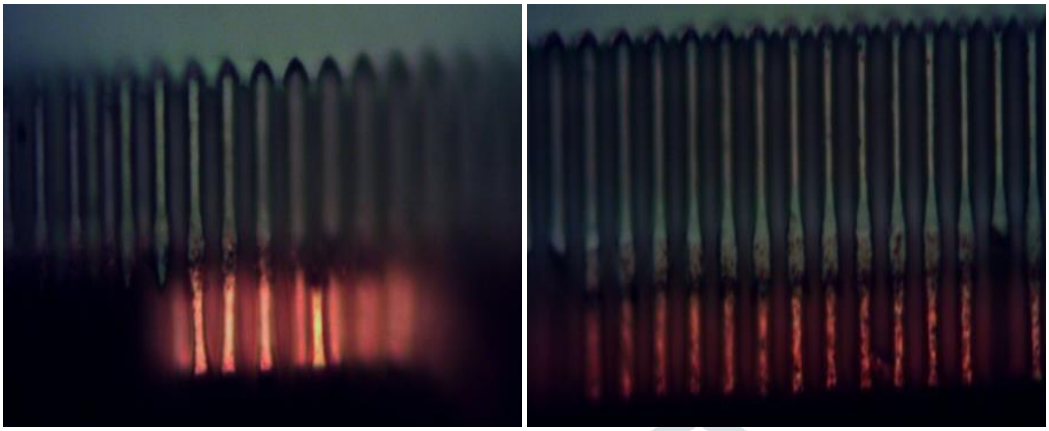
(c)

Fig. 9. Cu deposited on Si needles solution containing 3 g of $CuSO_4.5H_2O$ and 1 mL of HF (a) 0.5 g PEG (b) 1 g PEG (c) 2 g PEG.

For Sample B which is the best sample, electroless Cu deposition for solution containing 0.5 g of $CuSO_4.5H_2O$ and 4 mL HF at different PEG addition (0.5g, 1g and 2g) was also examined.

Copper was chemically deposited on three different Si needles by varying PEG addition. Formation of copper seed layer on the different wires varied accordingly with the amount of polyethylene glycol used. The chemically Cu deposited wires were compared based on the filling behavior of copper until the support layer formation of copper seed layer. Successful formation of copper seed

layer up to the support layer is observed as shown in Fig. 10. The inhibition effect of polyethylene glycol at small amount is negligible, as void free film of copper seed layer is formed. Hence, Fig. 10 (a) can be used as a current collector.



(a) (b)

(c)

Fig. 10. Cu deposited on Si needles solution containing 0.5 g of $CuSO_4.5H_2O$ and 4 mL of 48% HF (a) 0.5g PEG (b) 1 g PEG (c) 2 g PEG.

3.2. Mechanism of copper deposition

The effect of varying different parameters on electroless copper deposition has been performed. It is done in such a way that one parameter is varied while keeping the others constant. The copper deposited Si needles produced was compared based on the depth profile of copper filling, grains and homogeneity up to the support layer by considering 9µm from the top as a standard (see Fig. 1).

The depth of deposited copper on Si needles by varying different parameters was measured and accordingly, at higher depth values (greater than 15µm) deposition of copper has defects like voids or (seams). On the other hand, in some Si needles defect-free full deposited copper is obtained. This is done due to the fact that Cu ions diffuses faster at higher depth of the Si needles and reacts with the electrons released from the Si as result of the reaction with HF.

$$Si + 6F^{-} \rightarrow SiF_6^{2-} + 4e- \quad (3.2.1)$$

$$2Cu^{2+} + 4e- \rightarrow 2Cu \quad (3.2.2)$$

In most of lower depth values (less than 12µm) homogenous and defect-free deposition of copper up to the support layer is observed. This is obtained under the receipe of 4 mL of HF and 0.5 g $CuSO_4.5H_2O$ at 50°C and with 0.5 g of PEG addition that delays the faster diffusion of Cu ions in unwanted depth of the Si needles.

4. Conclusion

Electroless deposition of copper on Si needle arrays was accomplished and the deposition of Cu were more homogenous with a good coverage. As a result of Cu ions are totally consumed on the top and the availability of electrons, the deposition goes until the support layer and the needles were enabled to carry out current flows.

At higher amount of $CuSO_4.5H_2O$ used the electroless Cu deposition results with defects (seams and voids) this is due to the higher diffusion properties of the Cu ions easily trapped by the electrons that are released from the bath solution.

At low amounts of $CuSO_4.5H_2O$ and small amount of PEG c a homogeneous Cu film was obtained and deposited until the support layer with good coverage.

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