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Investigation of process parameters in electroless copper plating on polystyrene

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Abstract. There is a requirement of imparting conductivity to the surface of polystyrene for making various lightweight millimeter wave components. Researchers have worked on the plating of ABS material but there is very less work carried out on Polystyrene. This work has been carried out to make the surface of polystyrene conductive by electroless plating of copper on polystyrene followed by electroplating of copper. The acceleration process was added for increasing the acceptability of copper ions on etched surface. Test samples have successfully qualified rigorous grind saw test for checking adhesiveness of the plating layer. The samples were studied using a scanning electron microscope for the analysis of the morphology of the plated layer. Regression analysis of the different parameters was done for establishing the interrelation between the parameters. The results show that the achieved electroless plating on polystyrene is compact and continuous.

Keywords. Copper plating; electroless; electroplating; etching; adhesiveness; polystyrene.

1. Introduction

Polystyrene is a thermoset, rigid, translucent plastic produced by cross-linking. Polystyrene is used for the microwave industry. Polystyrene is electrically stable in the GHz frequency range. It is also optically clear, dimensionally stable and has excellent sound transmission characteristics. Polystyrene is often used for high-frequency circuit substrates, microwave components, etc. Polystyrene has a dielectric constant of 2.53 (up to 500 GHz) and exhibits an extremely low dissipation factor [1].

Copper plating of polystyrene substrate has enormous potential in the industry as it can be used to impart metallic properties to polystyrene surface which in turn can be used to make various types of high-frequency communication components and reflectors. Electroless plating has got outstanding deposition characteristics and this is the reason for its extensive use in the deposition of metal over various insulating substrates [2, 3]. The copper plating has been a widely used technology due to its low resistivity and high electro migration resistance [4, 5].

Different plating processes were studied for checking the interdependencies of input parameter variables and their effects on the final plating [6]. After plating by electroless process there is no requirement of sizing or machining, moreover, it results in uniform plating area [7, 8]. The reactions of electroless plating are catalytic and once started, they continue to plate metal [9]. The mechanism of deposition of a continuous film of metal particles in electroless plating is due to its autocatalytic nature which results in local deposition of metal [10].

Numerous successful attempts have been carried out in the field of electroless plating of copper on non-conductive materials like glass, PTFE, graphite and silicon carbide, etc. [11], but no significant work has been done on electroless plating of copper on polystyrene.

The traditional plating of metal by electrolysis requires degreasing, dipping in NaOH, dipping in HNO_3, etching by $SnCl_2$, activating by $PdCl_2$ and finally electroless plating [12]. Each of these stages is followed by rinsing by water. According to the literature, the biggest limitation of activation process involving palladium is its high cost which substantially increases the cost of plating [13], whereas, in the process of electroless plating of copper, the copper particles for the plating come from copper sulfate and formaldehyde (HCHO) acts as the reducing agent. Caustic soda (NaOH) controls the alkalinity of the solution (pH), compounds such as sodium-potassium tartrate keep the copper soluble in the solution and stabilizers, present in small amounts of 1–20 ppm, stabilizes the solution. It is the property of electroless solution, having metal ions and reducing agent, to cause a catalytic reaction over the pre-

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activated substrate. This results in an instant reduction of metal ions in the solution accompanied by the creation of the metal particles of colloidal sizes [14–16].

In the present research, experiments were conducted to stabilize the plating of copper on Polystyrene to achieve weight reduction of components with respect to their metal counterparts without compromising on other metal-like properties, for selective applications. The polystyrene samples were plated first using the established process of plating plastics [12] but the plating on the specimen surface continuously got peeled off, then one more process of treating the specimens using sulphuric acid solution (20%v/v) in distilled water was used for 3 minutes. The concentrations of all the solutions were varied for achieving a uniform and compact plating. The successful samples were further electroplated with copper.

Visual inspection was carried out to check for the plating quality. The morphology and structure of the electroless copper plating and electroplated copper are characterized by scanning electron microscope. For checking the adhesion of copper particles with the substrate Scotch tape test was applied [17] but finally, it was found that it will be better to use grind saw test, therefore, grind saw test was conducted to check the adhesion quality of the plated copper. Regression analysis was also carried out for establishing the relationship between different parameters on the success or failure of the electroless plating. The electroless layer achieved is defect-free and can be used as an interlayer for further electrochemical plating [18].

2. Materials and methods

The Rexolite (Polystyrene) which is a cross-linked thermoset polymer, was used as specimen material. Specimens, with an approximate size of 250 mm × 250 mm × 20 mm were prepared by cutting a large plate into pieces. It is already established that coarse surface can anchor the copper particles tightly resulting in better adhesion [19]. But as required for the application, one of the surfaces of 250 mm × 250 mm of each sample was machined to get a surface roughness of approx. 0.20 µm Ra value. Surface roughness of the samples under observation were measured using surface optical profiler, make: Bruker, model: Contour GT-KX, at 2.5x objective.

The process involved electroless plating of copper on polystyrene (nonmetallic) substrate, which comprised mainly of four sub-processes:

a. The etching process in which the substrate is treated with aqueous solution of stannous chloride acidified with hydrochloric acid.
b. The surface was activated using acidic palladium chloride solution so as to produce catalytically activated surface.
c. The treatment of the activated surface with acidic solution (Hydrochloric acid) for accelerating electroless plating of copper particles on the activated surface was done.
d. Lastly, electroless plating of copper was done through the reduction of formaldehyde on Cu^{2+} ions.

Prior to electroless plating various processes were performed to increase the surface area of the substrate by creation of pores and subsequently treating it with palladium chloride solution so as to create a metallic surface of palladium ions above the nonmetallic material to facilitate further electroless plating of copper (Fig. 1).

The temperature during the experimentation was measured using precision digital thermometer, make: ASL, model: F15, having least count 0.001°C and uncertainty ± 0.03°C.

Following sequence of operations were carried out:-

I. **Cleaning:** The important factors considered about cleaning process and cleaning solution were: concentration of cleaner, time in the cleaner, cleanliness, and rinsing after cleaning. Specimen were first treated with alkaline and then acidic solution to clean and neutralize the specimen. First, the specimens were treated with sodium hydroxide (10%) for five minutes then washed with distilled water and after that, they were treated with Nitric Acid (10%) for five minutes and at last washed thoroughly with distilled water.

II. Etching and Activation: This is the most important stage in plating process as it is fully responsible for

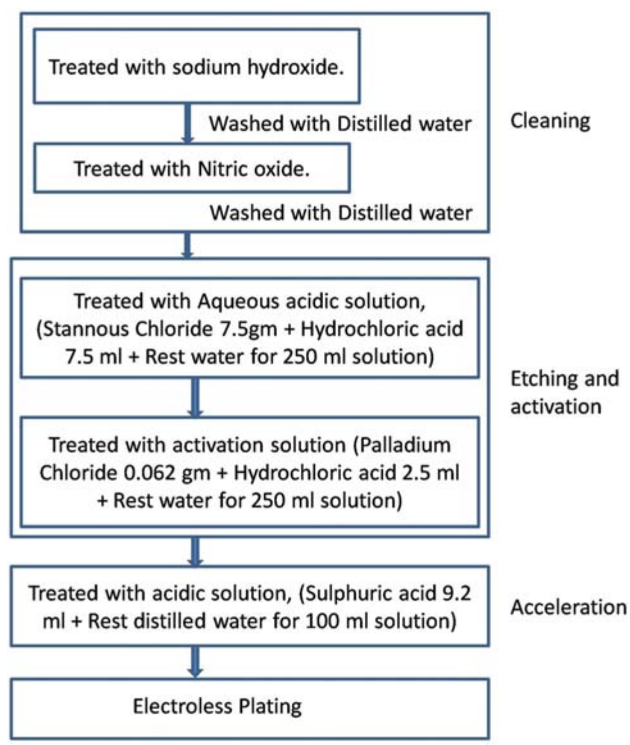

Figure 1. Sequence of Operations for Electroless Copper Plating on Polystyrene Substrate.

achieving suitable conditions for good metal polystyrene bonding. The parent surface is chemically etched resulting in the development of pores which can substantially increase the surface area of plating surface. The etched area served a number of purposes-

- An increase in the surface area, thereby providing more opportunity for intimate contact between metallic layers.
- A properly etched surface will provide anchoring sites for the activator material, which can mechanically bond to the metallic surface.

Activation was done using palladium chloride. In this process, palladium ions get deposited in the surface micro cavities (created by etching). An aqueous acidic solution was selected which has the following composition: Stannous Chloride 7.5 gm, Hydrochloric Acid 7.5 ml and rest distilled water for making 250 ml solution. The solution was aged for 24 hrs for achieving isotropic composition. The process takes place under the following conditions: temp. 27.5°C, pH 0.8 and process time of five minutes. After etching, activation was done using bath having the following composition: Palladium Chloride 0.062 gm, Hydrochloric Acid 2.5 ml and rest distilled water for making 250 ml solution. The process took place under the following conditions - temp. 27.1°C, pH 2 and process time of five minutes.

III. Acceleration: In this stage, the absorbed catalyst particles are activated to increase their activity. The accelerator used was Sulphuric acid. Acceleration of the palladium activated specimen was done using the following composition: Sulphuric Acid 9.2 ml and rest distill water for making 100 ml solution. The processing time was three minutes.

IV. Electroless Plating: An electroless plating layer is formed by a redox reaction on the activated surface. The formaldehyde and the hydroxide ions provide the reducing force necessary for the deposition of metallic ions. Plating was done on pretreated polystyrene sample using an electroless solution having following composition: Rochelle salt 172 gm/l, Copper Sulphate 35 gm/l, Sodium Carbonate 30 gm/l and Sodium Hydroxide 50 gm/l. The solution was aged for 24 hrs. The plating was done keeping two parameters fixed i.e. temperature 26.9°C and pH 13. The four parameters were varied –Time, varied from 25 to 360 seconds; the volume of electroless solution, varied from 98 ml to 24 ml, volume of distilled water varied from 1 ml to 75 ml and the volume of the formaldehyde, varied from 1 ml to 10 ml in the plating solution. A 100 ml solution containing the electroless solution, water and formaldehyde were used for each sample separately. The successfully electroless plated samples were first checked and then electroplated.

Visual inspection was done to check the uniformity of the plating. Scanning Electron Microscope (SEM) model EV018 (ZEISS, Germany) was used to check the quality and compactness of the plating of the specimen. The accelerating voltage was 20.00 KV, working distance was kept 6.5mm with magnification ranges from 5.21 to 5.25 (x 1000) times. For testing the adhesion of the copper plating on the polystyrene test piece, grind saw test was done on the samples. Regression analysis was done to establish a relationship between different constituents of solution and plating results.

3. Results

The influence of the variation of concentration of different chemical solutions and time of the process, on the plating quality was studied. Results are as explained as follows.

3.1 *Surface morphology*

Firstly, electroless plating specimen were studied and it is evident from figures 2, 3 and 4 that as the process got stabilized, there is uniformity in the position and orientation of the copper particles above polystyrene samples.

Figure 2 clearly shows lack of cohesiveness between copper particles during initial experiments of electroless plating.

Figure 3 clearly shows improvement of cohesiveness between copper particles during further experimentation of electroless plating.

Figure 4 shows marked improvement of cohesiveness between copper particles during final experimentation for electroless plating.

The study revealed that the surfaces of the samples under test were evenly covered by copper particles and there were no apparent defects and openings on the coated surface. The successfully electroless plated samples were then

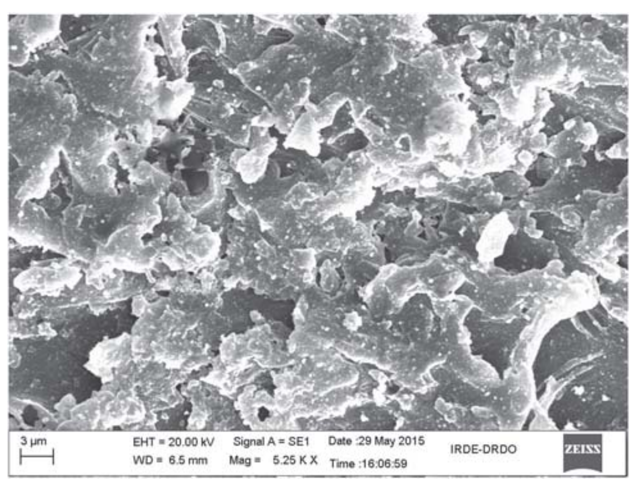

Figure 2. Initial poor results in Electroless Plating.

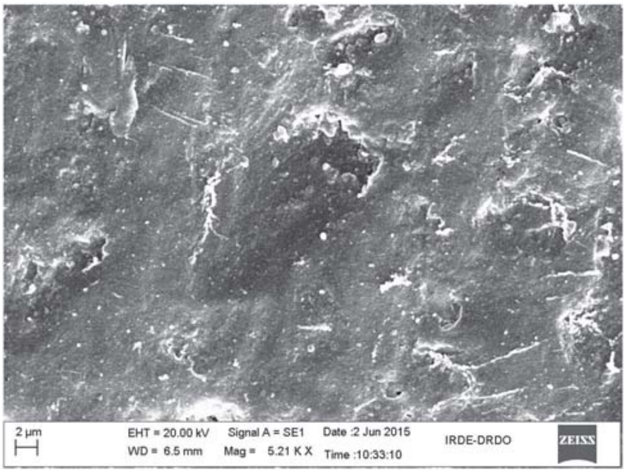

Figure 3. Marked Improvement in Electroless Plating.

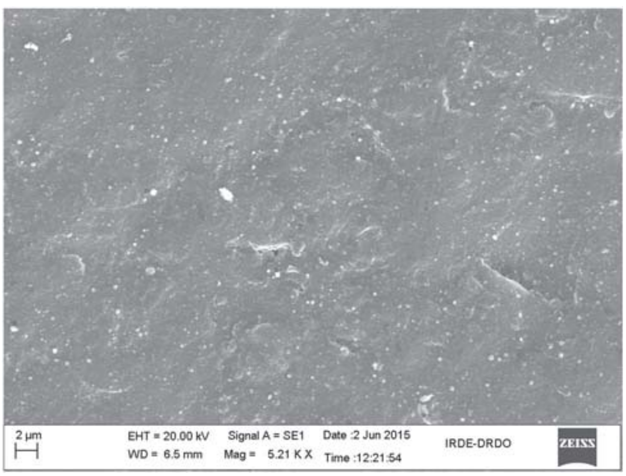

Figure 4. Stabilised Electroless Plating.

electroplated with copper for thirty minutes and then were analysed by SEM. It is deducible by the images on Figure 5, 6 and 7 that the grains of copper deposited over specimen are round in shape and there is a uniform distribution of copper on the substrate.

Figure 5 shows an uneven distribution of copper particles and size variation on poor electroless plated surface, corresponding to figure 2, during copper electroplating.

Figure 6 shows a somewhat better distribution of copper particles and lesser size variation on improved electroless plated surface, corresponding to Figure 3, during copper electroplating.

Figure 7 shows a far better distribution of copper particles and minimal size variation on good quality electroless plated surface, corresponding to figure 4, during copper electroplating.

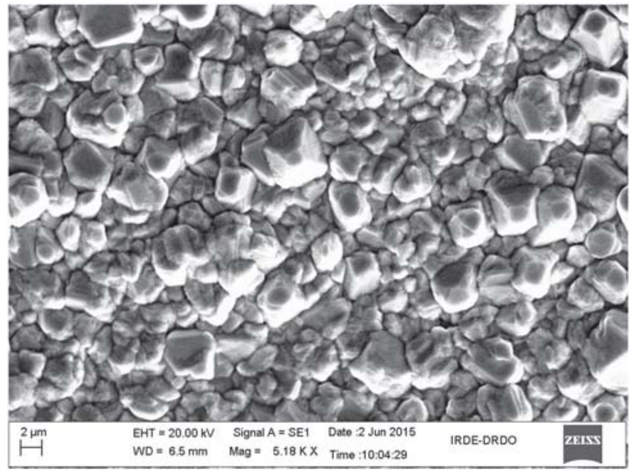

Figure 5. Copper Electroplating on the Sample corresponding to figure 2.

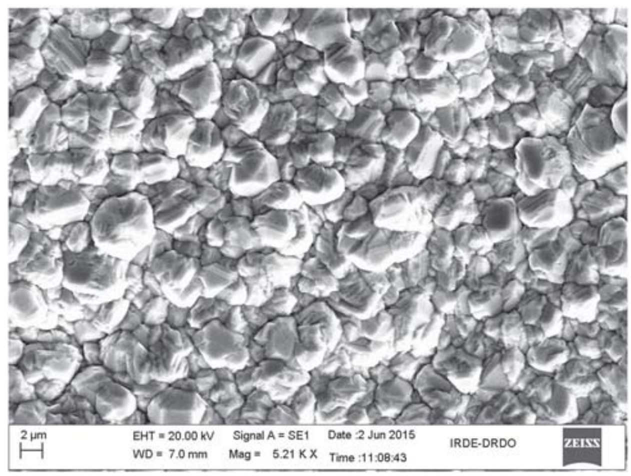

Figure 6. Copper Electroplating on the Sample corresponding to figure 3.

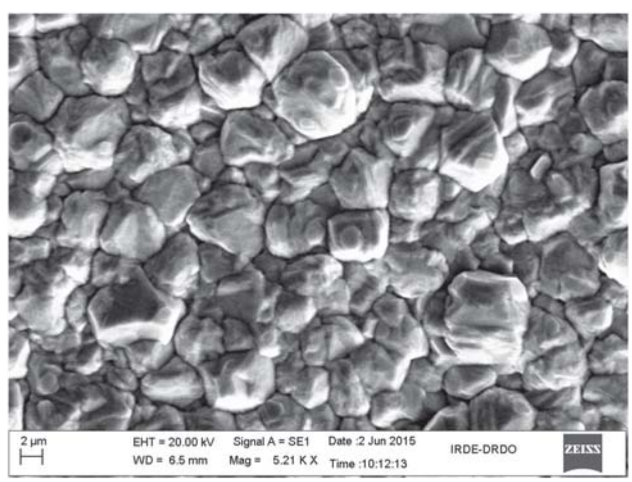

Figure 7. Copper Electroplating on the Sample corresponding to figure 4.

Results of SEM shows material was evenly deposited on the surface proving success of electroless copper palting on substrate [20]. Uniform and continuous plating of copper particles over polystyrene samples is due to reduction in the concentration of formaldehyde which makes the reaction more stable. Progressively the solution was diluted with distilled water and at 75% dilution i.e., 75 ml water, 24 ml electroless solution and 1 ml formaldehyde, resulted in successful plating.

3.2 *Grind Saw test*

For checking the adhesion of the copper particles on the polystyrene substrate, Grind Saw test was done on the samples in which the samples, after electroless plating, were sawed using hacksaw across the plating into two pieces. A hacksaw was used for sawing the specimen in the direction that tends to separate the coating from the substrate. Lifting or peeling of plating is the evidence of unsatisfactory adhesion.

Figure 8 shows that the metallic copper layer was not peeled off during Grind Saw test across the electroless copper plated polystyrene specimen. It indicates the excellent adhesiveness of copper plating over the polystyrene substrate.

3.3 *Regression analysis*

Regression analysis establishes the correlation between a dependent (response) variable and one or more independent variables. As in this case, there are four parameters upon which the quality of plating was dependent but the outcome or response variable was only one. Either the plating will be successful or failure (peeling), so in order to determine the contribution of each parameter a regression analysis was done using Minitab 17 software. The predictors selected were-volume of formaldehyde (HCHO), the volume of distilled water (H_2O), volume of electroless solution (E.Sol) and the processing time of electroless plating (Time); and the

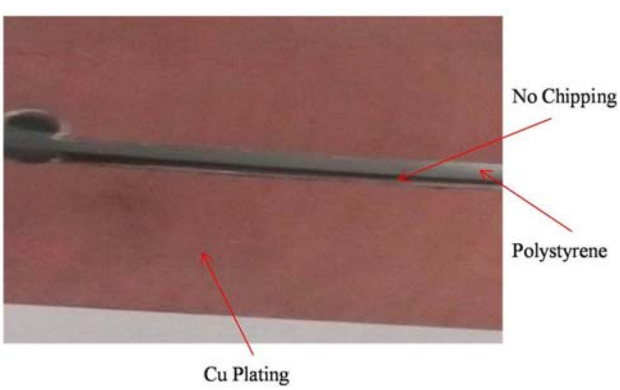

Figure 8. Sawed Pieces After Electroless Plating.

response was the dichotomous i.e., success (denoted by 1) or failure (denoted by 0) for the electroless plating. The residual value of the parameter is the difference between the best-obtained value obtained by the regression equation and the observed value obtained through the experiment. The graphs obtained after regression analysis are shown in figure 9.

Equation (1) confirms that the volume of electroless solution and volume of water are determining factors in successful electroless plating under consideration. The process of acceleration with sulphuric acid makes the substrate highly susceptible for plating, however sulphuric acid has not been considered in regression analysis as it has been taken as constant factor.

3.3a *Normal probability graph of residuals*: The distribution of residuals should show a regular variance and it should generally form a straight line if the residuals are normally distributed; it is clear from the graph that there is a fairly good approximation for normalcy. The linear pattern is consistent with a normal distribution.

3.3b *Residuals versus fit*: The plot of residuals versus fitted values is in conformance with normal probability plot and shows that residuals get larger as the fitted value increases, which indicates that the residuals have constant variation.

3.3c *Histogram of residuals*: The histogram is an explanatory tool to indicate the statistical distribution of the data including special values as well as the spread of the data. If the histogram plot is compared with the normal probability curve it is found that during the start and towards the end, plot values deviate appreciably from the normal distribution, indicating that there are outliers in our experiment i.e. some extreme values of parameters, beyond which the quality of plating cannot be improved keeping all the remaining parameters constant.

3.3d *Residuals versus order*: The graph (Figure 9) shows all residuals in the order in which the data was gathered and is utilised to obtain non-random error, it is evident from the graph that there is no cluster of data which implies uniformity of values. A total of thirty experiments were recorded and analyzed using Minitab 17 for regression analysis. The obtained regression equation is:

$$\begin{aligned} \text{Rating} = & -1.61 + 0.0195\,(\text{E.Sol}) + 0.0289\,(H_2O) \\ & -0.0247\,(\text{HCHO}) - 0.00339\,(\text{Time}) \end{aligned} \tag{1}$$

4. Discussion

The properties of electroless copper deposits are based on their microstructure characteristics. Studying the microstructure of the deposits helps us to understand the mechanism of deposition and evaluate the properties of

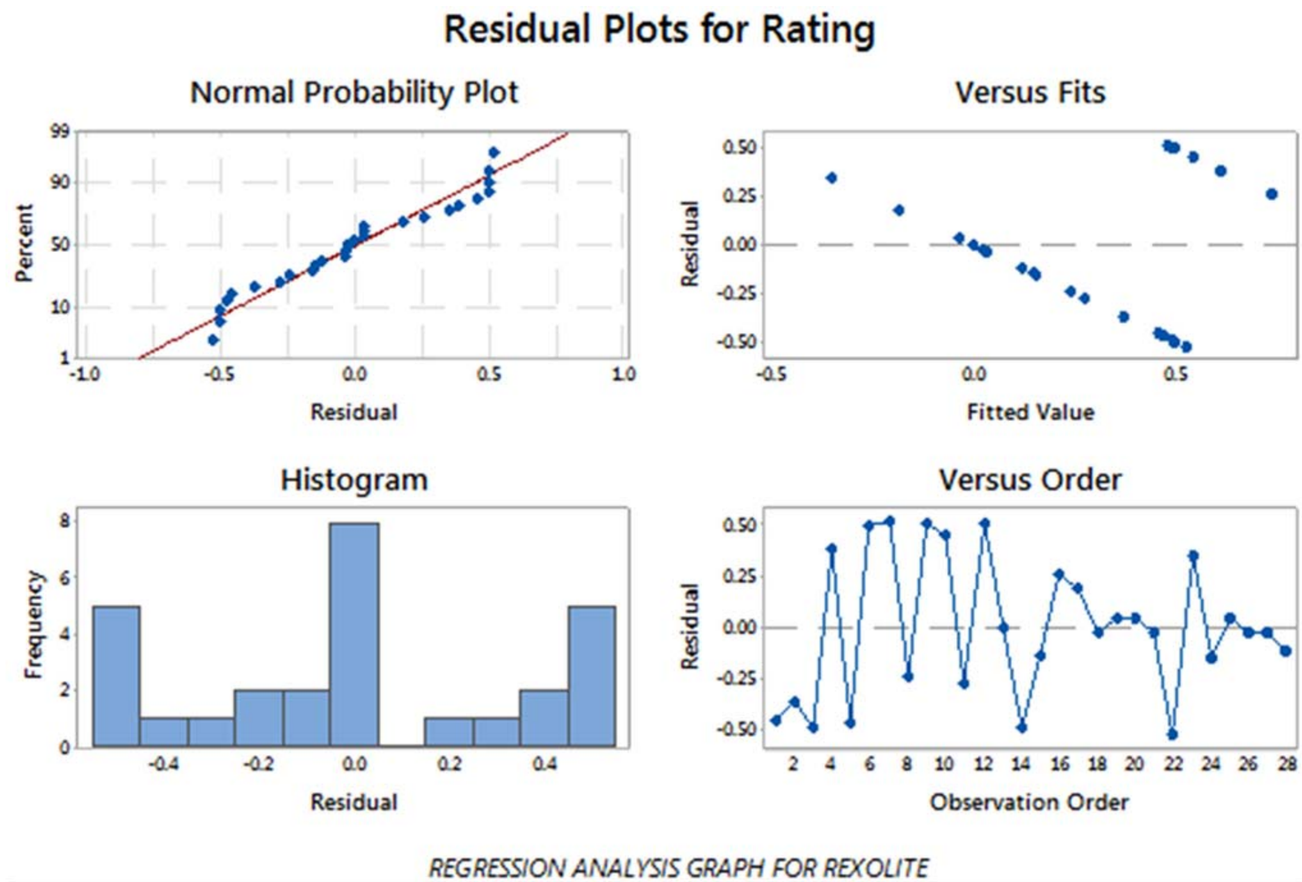

Figure 9. Regression Analysis Graph (Polystyrene).

copper deposits. From figures 2, 3, 4 and 5, 6, 7 it seems that the surface of the polystyrene samples was compact and continuously covered by copper particles and there were no obvious flaws and apertures on the coating surface The SEM analysis of samples clearly shows that as the surface quality of electroless plating improves, the distribution of copper particles become uniform.

4.1 *Effect of change in volume of formaldehyde*

Formaldehyde acts as a reducer for the electroless plating reaction. To make electroless plating reaction stable and to achieve a uniform as well as continuous plating of copper particles over polystyrene, the concentration of formaldehyde was reduced progressively from 10 ml to 1 ml for making 100 ml solution for electroless plating. It was found that the electroless plating of copper over polystyrene was very vigorous with a higher concentration of formaldehyde resulting in peeling of copper plating.

4.2 *Effect of change in volume of electroless solution*

The deposition of copper on the etched surface of polystyrene takes place through the availability of copper particles in the electroless solution. It was found that the solution, when used in the initial concentration, leads to peeling of copper plating, it seems that over availability of copper particles resulted in such a flaw. When the volume of electroless solution was progressively reduced from 98 ml to 24 ml for making 100 ml solution for electroless plating, it resulted in successful plating of copper particles on Polystyrene substrate.

4.3 *Effect of electroless plating time*

While experimenting, it was found that a threshold value of 25 seconds was crucial because below this the process of copper plating did not initiate at all but after crossing the threshold, time did not play an important role in the plating process. Therefore the time for electroless plating was analysed and finally reduced from 360 to 25 seconds and it

Table 1. Extreme Values of Input Parameters.

Sl.no.	Parameter	Lower value	Upper value
1.	Volume of Electroless solution in prepared solution	24 ml	98 ml
2.	Volume of water in prepared solution	1 ml	75 ml
3.	Volume of formaldehyde in prepared solution	1 ml	10 ml
4.	Time (Electroless plating)	25 seconds	360 seconds

was observed that 75 seconds of electroless plating time yields desirable results. Which got reflected in saw test of the specimen where it was observed that there is no chipping of copper film. Time has very little correlation with the electroless plating quality as compared to other parameters.

4.4 *Analysis of regression equation*

The slightly positive coefficient of electroless solution concentration means that the success of plating is weakly but positively related to the concentration of the electroless solution and the plating can be improved by increasing the dilution of the electroless solution up to 24 ml in 75 ml distilled water.

A positive coefficient of the volume of water in the prepared solution implies that with increase in the quantity of water, the stability of plating can be improved. A negative coefficient of the concentration of formaldehyde on the electroless solution states that to get stable copper plating on polystyrene, the concentration of formaldehyde should be kept low. The plating time is very weakly and negatively correlated and does not seem to affect plating quality as such. Table 1 shows the extreme values of the parameters under consideration. Figure 9 shows the graphs obtained by the regression analysis using Minitab 17.

Problems encountered during various processes, their causes and solutions used to overcome the problems, are as under:-

Etching-

- Parts etched were very light in appearance, the identified reason is less agitation of solution which was corrected by increasing the agitation.
- Parts surface was very rough, the identified reason is contaminated bath. For correcting it bath solution was filtered.

Acceleration-

- No plating at all, the identified reason is contamination which was corrected by cleaning the bath.
- No plating on the sample edge, the identified reason was over acceleration which was corrected by altering the agitation speed.

Electroless plating-

- Plated surface was rough, the identified reason was particulates in bath, it was corrected by filtering the bath and agitating the specimen.
- The bath was overactive, identified reason was high reducer and low stabilizer concentration which was corrected by altering the concentration.
- Sluggish bath, the identified reason was pH out of range and low reducer concentration which was corrected by stabilizing pH and increasing reducer concentration.

5. Conclusion

The results of this investigation suggest some important conclusions, which can be summarized as follows.

1. The addition of the accelerator process using sulphuric acid solution (20% v/v) in distilled water for 3 minutes makes the process more acceptable for electroless plating of copper on polystyrene substrate.
2. The concentration of electroless solution prepared for copper deposition on polystyrene substrate and the concentration of formaldehyde are the determining factor behind plating quality. The 75 ml distilled water dilution with 1 ml formaldehyde and 24 ml electroless solution resulted in successful plating and yielded optimal results.
3. At these deduced values of the selected parameters, the adhesion of copper with polystyrene was good as analysed by the Grind saw test and SEM images.

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