Chapter 2

Literature survey

2.1 Introduction

The current chapter highlights the different types of surface conditioning for electroless metallization and their demerits. To avoid the use of toxic etchants as well as high cost palladium different environmental friendly metallization processes are discussed.

2.2 Electroless metallization

Surface conditioning is very much essential for electroless metallization on plastic before deposition. Among the different surface conditioning operations, etching and activation are the most significant steps for electroless deposition especially for copper. Etching is a surface conditioning process which makes the surface the porus that increase the surface area of the part material and this is essential for good adhesion between metal and plastic. Activation stage is more important for electroless Cu deposition. In this operation the activator particles get deposited into micro cavities which were formed by etching stage.

Equbal and Sood [1] were used H_2SO_4 and CrO_3 acid separately for etching before electroless Cu deposition on ABS parts. For electroless plating they used four acdic baths namely HF, H2SO4, H3PO4 and CH3COOH with different deposition time. They found that conductivity as well as Cu deposition was obtained in all baths except CH_3COOH and better result in terms of uniform deposition in H2SO4 bath due to large availability of hydrogen. They observed that with increase in deposition time, conductivity as well as copper deposition was gradually increased. Among the two etching solution, they found that electrical performance and Cu deposition shows better result in Cr2O3 acid etchant in all baths. Another process of direct copper plating in ABS surface was investigated by **Gui-xiang et al. [2].** They used CrO_3/H_2SO_4 as etching solution with activation by Pd/Sn colloids solution and accelerated with solution containing NaOH, $CuSO_4.5H_2O$, and

EDTANa2 before copper electroplating. They found that Pd/Sn colloid catalyst have good dispersivity with narrow distributing of particle size. Due these smaller particles of catalyst, the dispersivity as well as the activation gives good result. They found that due the disproportionation reaction of Cu2O, metallic copper particles form on the Pd particles. So this results uniform copper deposition over the ABS parts due to the use of Pd/Sn colloid catalyst which having good dispersivity. **Luan et al. [3]** carried the chemical surface preparation for electroless metallization of stereo lithography polymers. For etching solution they used chromic acid and sulphuric acid. In that experiment they conducted the contact angle analysis for assessing the surface hydrophilicity to optimize the preparation process. The results show the applicability of this technology by subsequent metallization process. So it was as an efficient method for metallization of SLA polymers. **Hong et al. [4]** have investigated on autocatalytic electroless copper deposition by Palladium activation with dc magnetron sputtering of tantalum and tantalum nitrides (TaN_X) with different nitrogen content. They found that phase transformation on the deposited TaN_X film with the addition of small amount of nitrogen. With the increase of nitrogen flow rate, the electrical resistivity of the TaN_X deposited films first decreased for the nitrogen flow rate up to 10 standard cubic centimeters per minute (sccm) and then increased for nitrogen flow rate of more than 20 sccm. They also found that the density of palladium nuclei increased with the increase in nitrogen content and the grain size of TaN_X films decreased with the increase of nitrogen flow rate. **Ono et al. [5]** have studied the direct plating of copper on non-conducting resin substrate. Here Pd/Sn mixed catalyst was used to catalyzed the ABS resin substrate and was accelerated in copper ions solution before the direct plating. Due to the migration of direct Cu plating cubic Cu_2O crystals were formed with approximate size of 10-20 nm. The Cu_2O crystals were enhanced the copper deposition by the generation of additive free metallic copper.

The chemical etching of poly (ether ether ketone)/ carbon fiber composites by Cr_2O_3/H_2SO_4 solution performed by **Di et al. [6]** followed by electroless plating with copper ant after that electroplating with nickel. They have studied the effects of chemical etching time and temperature on the adhesive strength of the PEEK/Cf and Cu/Ni layers. They found that the C=O bond increased after chemical etching. More cracks and partially exposed carbon fibers appeared on the surface of the composite with increased in etching temperature and time. Also the electrical resistivity of the metallic layer increased with the increased in etching temperature and time. The composites with etched by temperature at 60^0C for 25 min and at 70-80^0C for more than 15 min have with stand four thermal shocks cycles without bubbling. **Debarnot et al. [7]** have investigated the influence of the polymer pretreatment before the electroless pretreatment. In this work they have used mixed Pd-

Sn colloidal solution for the activation of polyvinylidene fluride (PVDF) surfaces for copper deposition. Here plasma pretreatment was used in presence of N_2 or N_2/H_2 reactive gases. The different parameters to prepare the colloidal solution were reaction temperature, growth time of colloids, plasma processing conditions to obtained metallic palladium with high concentration and good adhesion of copper on the PVDF surface.

2.3 Electroless metallization without use of palladium

To avoid the use of toxic acids in etching process and use of high cost Pd in activation step, a lot of research is going to find environment friendly metallization. **Bazzaoui et al. [8]** investigated a process of copper plating on ABS surface by using polypyrrole. Before copper plating ABS parts were immersed in a solution of 0.3M pyrrole and 0.9M $FeCl_3$. After polymerization the parts were electroplated by using a bath containing $CuSO_4$ $5H_2SO_4$, H_2SO_4, CUFLEX 500 MU base with a 4 cm2 copper wire. This process replaces the use of etching solution as well as use of Pd/Sn catalyst and here the researcher used only one process i.e. the polymerization before electroplating. **Tang et al. [9]** have performed a new surface activation process for electroless Ni/Au plating on ABS plastics. It is Pd-free activation process for the electroless metallization on the ABS plastics that reduced the cost of production. Here the ABS plastic surface was first immobilized by Ni (0) nanoparticles by chitosan (CTS) film followed by deposition of NI and AU on the ABS plastics. Here Au layers were found on the top surface of the Ni layers with stable non-cyanide electroless Au plating. **Qian Ma et al. [10]** investigated a method which replace the use of high cost palladium for activation. They etched ABS parts with a solution containing MnO_2, H_3PO_4 and H_2SO_4 and before this they swelled the parts with tetramethylammonium hydroxide (TMAH), and 1-Methyl-2-pyrrolidinone (NMP) for better etching. Then the substrates were activated with CATAPOSIT44 solution before electroless Cu deposition and electroplated to increase Cu thickness. They studied the surface topography due to swelling and found adhesion strength of 1.04 KNm^{-1} for electroless copper film.

Tang et al. [11] have performed a new method of metallization Ni on ABS plastic. They have used a new palladium free and environmentally friendly surface characterization of Ni by electroless plating on ABS plastic. The surface activation was performed successfully by the immobilizing Ni nanoparticles as catalyst. From the SEM photograph of the Ni plated ABS plastic it was found that Ni nanoparticles were uniformly generated on the substrate with a glossy and smooth Ni-P plating layer. This environmentally friendly metallization process reduces capital cost as well as operational cost in large scale production. **LI et al. [12]** investigated an electroless copper deposition method

without the use of etching and Pd/Sn catalyst. They used Al-C paste as a surface pretreatment process before electroless deposition in four different baths such as H2SO4, H3PO4, HNO3 and CH3COOH. They compared results with different deposition time at room temperature and at 60^{o}C of different electroless baths. They founded that except HNO3 bath all baths are capable of formation of Cu crystals and conductivity. H2SO4 and H3PO4 baths gives better result compare to other baths in terms of size of Cu crystals and electrical performance due corrosion of Cu and over-etching of Al seeds by HNO3. They observed that except HNO_3 bath and better result at 60^{o}C compare to room temperature. **Shu et al. [13]** investigated an environment-friendly technics which substitute the use of Cr_2O_3 for etching as well as Pd/Sn catalyst for activation. They used a solution of sulphuric acid and magnesium oxide (H_2SO_4-MnO_2) as an etching solution. They also observed that copper can be successfully deposited on ABS parts by using $CuSO_4$ and with reduction of DMAB (dimethylamineborane, $(CH_3)_2NHBH_3$) which indicates that this process can replace the use of high cost palladium in activation process. They measured the adhesion strength with different temperature and get average adhesion of 1.31KNm^{-1} at 50^{o}C. **Naruskevicius et al. [14]** investigated a Co-based surface activator for electroless metallization of copper on ABS surface. They proved that with the use of colloidal cobalt solution, Co ions can be seeded into the ABS surface which can be able to initiate electroless copper deposition without the use of high cost palladium. They found that due to the presence of a small amount of Cu2+ ions in the colloidal Co-based solution, which catalyzes the reduction based on the dielectric surface producing Co (0) seeds which initiate electroless copper deposition.

A new surface treatment method was developed by **Magallon-Cacho et al. [15]** which can avoid the use of environmental unsuitable CrO_3. In this method they used photocatalytic reaction of TiO_2 on ABS surface. They founded that due to generation of TiO_2 nanoparticles on ABS surface 30µm thick Cu can be developed with excellent adhesion strength. **Luo et al. [16]** investigated a method of copper deposition on PC engineering plastic. They developed a new method of activation process that replace the conventional sensitization and activation (i.e. use of high cost palladium) stages by using aqueous solution of nitric acid, hydrogen peroxide and NH_4F. In that mechanism they analyzed that the reactant (Cu2+) present in the electroless solution was distributed and absorbed by the plastic parts. At a result they founded similar morphology of copper layer as compare to conventional pretreatment process.

2.4 Summary

From the above literature survey different surface conditioning process for electroless are studied. For etching, normally chromic acid (Cr_2O_3) or sulphuric acid (H_2SO_4) are used. But these acids are toxic and hazardous to environment. The conventional surface activation process used a solution containing $SnCl_2$ and $PdCl_2$ for sensitization and activation. Due to high cost of palladium, the process becomes very expensive. Hence, respecters found some environment friendly electroless metallization is preferred because it eliminates etching as well as the use of palladium (Pd).