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Electrodeposition of Nickel into Molds produced via Rapid Prototyping

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Abstract

This research investigates the opportunities and limitations of the electrodeposition of nickel onto a rapid prototyped mold. Selective electroplating onto a rapid prototyped mold shows promise for smaller, more flexible design of integrated circuitry and nanotechnology. The circuit pathways and the transistors on today’s integrated circuits constitute the majority of a circuit's volume. The transistor consistently decreases in size, but the circuit pathways fail to keep up. To test the electroplating capabilities of the Stereolithography Apparatus (SLA) Quickcast technology, small discs with varying conic cutouts were electroplated using nickel. All of the discs have varying angles with dimensions on the micrometer range. Seed layers were utilized to provide conductivity on the surface of the mold and to decrease the size of the conic holes. A variety of seed layers were examined, including a gallium indium eutectic, a deposited graphite solution, and silver layering. While the layerless setups have a direct connection to the copper plates, the seed layers provide conductivity to the surface of the mold by painting a conductive pathway to outside of the platable surface. Nickel plating then electrodeposited onto the surface of the copper plates or seed layer, depending on the experimental setup. Unfortunately, most of the tests in the study yield unsatisfying results for various reasons, ranging from surface roughness to conductivity. Some select experiments gave positive results such as silver seed layering, although the process took several days to complete. As a result of this research, rapid prototyped technology could contribute to integrated circuit design and development.
Keyword: Rapid Prototyping, Electroplating, Nonconductive surfaces

1. Introduction

Research and development teams use prototypes to save money and therefore increase efficiency, something made ever more accessible by rapid prototyping. Rapid prototyping is a fast and efficient way to create a physical model of an object for review and study before taking further steps in the production process. Parts created using rapid prototyping share a number of additional benefits, including the ability to create seamless parts and the freedom to create parts which cannot be fabricated using other methods with ease. Another important technology that emerged arguably over two millennia ago, is electrodeposition. Many fields benefit from electrodeposition and electroplating, from jewelers to computer chip manufacturers. Many companies and individuals plate material onto others to increase mass or to change their outer properties. This report explores the opportunities and limitations of electroplating onto rapid prototyped molds, to allow future improvements, as well as more extensive tests. Nonconductive alumina filters have been used as molds for electrodeposition[1]. Nanowires are made by electroplating onto a selected surface controlled by a dissolvable film with a series of microscopic pores. A similar method is explored in this study.

1.1. electrodeposition

Oxidation-reduction (redox) reactions involve the transfer of electrons. A redox reaction requires that one element gains electrons (reduction) and one element loses electrons (oxidation). If a system is set up correctly, electrical current can be used to deposit one material (that being reduced) onto another surface. Reduction refers to the reduction of positive charge that result from adding electrons to a system, which thus produces negatively charged ions:

$$Ni + 2e^{-} \rightarrow Ni^{-2} \quad (1)$$

On the other hand, oxidation increases the charge of the element by losing electrons:

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

Thus, the electrical current has caused these two otherwise unreacting materials to contain attracting ions. If placed within an ion bath of nickel plating solution, the ions from the solution will plate the copper in an attempt to balance the charge of the copper ion's positive charge. As a result, nickel ions will break away from the solid piece to replace the ones lost in the nickel ion solution. The reaction taking place sometimes requires a certain amount of energy, depending on whether the reaction is spontaneous or not. Nonspontaneous reactions require energy, whereas spontaneous reactions occur naturally. Therefore, when a nonspontaneous reaction needs to occur, the user needs to input a certain amount of energy into a system, usually in the form of a power source. Specifically, the reaction above requires -0.59V to take place, translating to a battery of greater than 0.59V output with its positive end closest to the lead rather than the nickel wire.

1.2. nonconductive surfaces

Electrodeposition requires electrical conductivity because electrons need to be transferred to the material to be coated with the electrodeposited layer. Electrically conductive surfaces make this possible, because nonconductive surfaces do not allow sufficient electron flow.

1.3. seed layers

One way to route around the nonconductive surface this research deals with is to introduce a seed layer. According to the report "Damascene copper electroplating for chip interconnections", IBM stated that "it is first necessary to cover the surface with a seed layer, or plating base, whose function is to conduct the current"[2]. This concept and method of seeding a material onto a surface greatly increases the accuracy and precision of the electroplating process. However, the accuracy of the placement of the seed layer comes with its own margin of error, depending on the materials used.

1.4. mold geometry

In this project, several geometries were considered for the mold's deposition pattern. Many geometries were discarded due to not being able to quantify the success of the plating, such as an L cutout or spiral cutout,. Ultimately, conic cutouts became the object of study for two reasons. The first being that only one variable needs to change from mold to mold, or the angle of inclination. Secondly, these angles could correlate with the level of electroplating using a microscope. Ideally, the slope of the mold would change after the electroplating process. Certain limits came into play using the SLA technology to create the molds. Accuracy presented the most obvious limitation. The SLA technology has a one tenth of a millimeter accuracy, with anything smaller not building properly[3]. Figure 1 below is a conic mold with a 2.5mm diameter hole. This measurement helped guarantee an accurate build for all molds constructed.

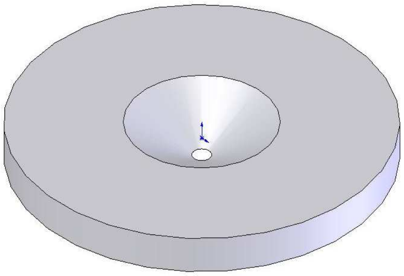

Figure 1. Solidworks model a conic cutout with 30° angle of inclination. The entire structure is 5mm tall and 28mm in diameter.

1.5. rapid prototyping

Rapid prototyping makes concepts and design easier to conceive for faster and more efficient application of products and ideas. Additionally, rapid prototyping allows for near unbridled freedom in design, pushing the limits of complexity of parts produced, simply because of the way they are produced, which is layer by layer. This research takes advantage of SLA (steriolithography) technology, which uses a liquid resin polymer. When a laser focuses on a specific point of the resin, it “cures” and becomes a solid at that specific point. After the laser cures several points, usually in the hundreds or thousands, the cured layer will drop down deeper into the vat of resin, exposing a fresh new liquid layer for the laser to cure. After several layers cure, the now-cured polymer possesses a certain shape matching the user’s specifications generated in any modern CAD software.

2. Methodology

2.1. electrodeposition

It is important to understand the general flow of electrons and its impact on the deposition process: in this case, the battery will cause electrons to flow towards the copper bar, and pull them away from nickel (Ni) coil. This first facilitates the nickel plating solution to give up its nickel ions (with a +2 charge) to balance the copper bar’s negative charge (-2) by forming a weak bond to the surface of the copper. The nickel coil produces nickel cations with a +2 charge after loss of electrons, as in the plating solution. Loss of electrons degrades the Ni coil and the Ni cations are donated to the nickel plating solution. In the case of the seed layer, the nickel should deposit to the seeded layer, which then completes the circuit.

Two experimental strategies were developed and explored through the course of the research, one being a direct copper lead connection. This does not utilize a seed layer, nor does it have to. As figure 2a shows, the nickel ions deposit onto the copper directly, with the prototyped mold controlling the overall shape. Theoretically, this builds layer by layer from the bottom up, following the pattern outlined, leaving no problematic gaps sometimes encountered when plating sharp-angled surfaces, such as boxes. The current to facilitate this process must flow to the nickel, such that the positive end of the voltage source should be closer to the nickel.

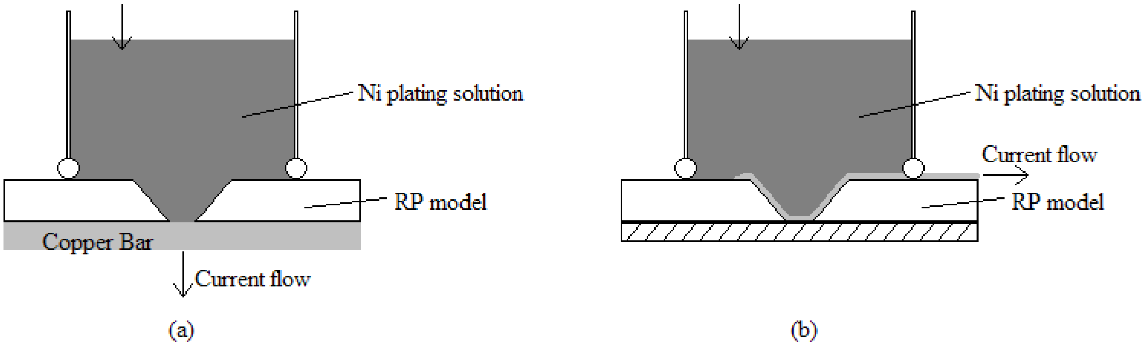

Figure 2. a) First experimental setup; direct copper lead connection to nickel plating solution.

b) Second experimental setup; electroplating circuit completed through seed layer.

Figure 2b outlines a setup using a seed layer of graphite to direct electrodeposition onto specified regions of the mold. As mentioned above, this creates certain undesirable results, such as superdeposition, which leaves pockets of unplated regions across the surfaces or crevices of interest. Moreover, the second method described requires additional preparation and chemicals to carry out, as opposed to the simple copper lead of the first. First, the following aqueous solution is formed (by mass): 4% graphite powder with particle size <20µm, 1% sodium silicate, 0.5% lactic acid. Ammonia was then added to adjust the pH to 10. The ammonia acts as a buffer for subsequent steps in the seed deposition process. To add the seed layer, the prototyped model should submerge into the graphite solution for 2 minutes. Immediately after, the model then is placed in a 6M Hydrochloric Acid bath for 90 seconds. Then, after any excess water is removed through heat and evaporation, the electroplating process can proceed.

Figure 3 illustrates the apparatus and general setup of both experiments described above. Both include a plastic surface with the prototyped mold placed on top, followed by a rubber ring to prevent leakage. The final piece is plastic tubing with wings that overstretch the rubber stopper. These wings support clips that create a seal for the liquid nickel plating solution. In the first setup with the direct copper connection, a copper bar separates the base and the prototyped model, whereas the second experimental setup does not require this. The second setup clips directly to the mold, thus forcing the current to flow through the mold.

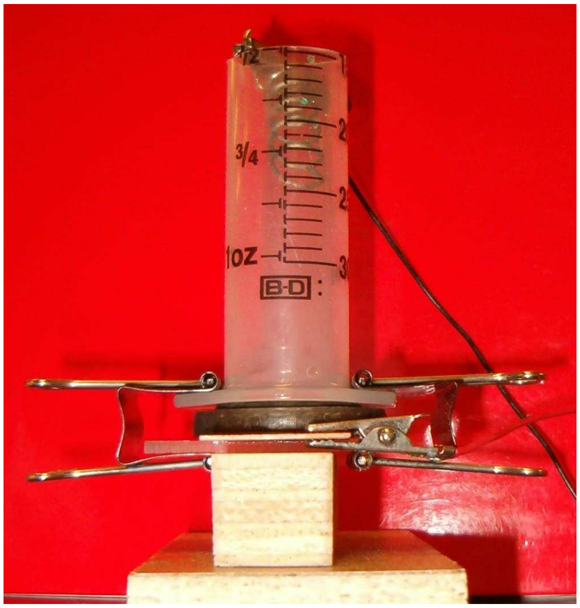

Figure 3. General setup for electroplating experiments, specifically the first described.

Figure 3 displays the experimental strategy. To electroplate the mold, 3 Volts (2 AA batteries) in series should connect to the nickel wire (which is half submerged in the plating solution) and the lead, which will either be copper or a gator clip clamped to the side of the prototyped mold. Each experiment should be run for 4 hours.

2.2. seed layers

There were three setups: one utilizing a seed layer of either GaIn, graphite solution, or silver, one using the a copper plate stationed below the prototyped mold such that the nickel deposited in layered fashion through the mold, and a hybrid of the two, which utilizes the copper for circuit contact, but also possesses the seed layering. All utilized similar apparatus to electroplate the said surfaces. Particularly, the equipment to complete the electrical circuit, which drives the electroplating process, remains the same. The copper plate connects via gator clip to a copper wire, which feeds into the negative terminal AA battery housing. The battery's positive end then feeds into another gator clip, which holds a coiled nickel wire, feeding into a nickel plating solution.

The first seed layer, composed of GaIn eutectic painted onto the mold. After being painted on, a bridge to outside of the rubber ring painted onto the prototyped mold so that the circuit could be completed without interfering with the reaction.

U.S. Patent 5547558 outlines a process for electroplating nonconductive surfaces using a graphite solution. For the experiments performed, only the size of the graphite particles differs from the patent's specifications. The patent described uses small graphite particles no larger than 2μm in diameter, whereas the following results were produced from experiments using graphite particles no larger than 20μm in diameter[4]. To counter the problem of size (and therefore decreased material conductivity), the electroplating process was allowed to run longer. Additionally, a slightly higher voltage facilitates faster material flow because the increased electron flow will increase the number of ions available for electrodeposition.

The silver layer was made using an experiment to exemplify hydrophilic and hydrophobic reactions[5]. Using a solution of 10 mL silver nitrate, concentrated ammonia was added dropwise until the solution became clear. Shortly afterwards, 5 mL of Potassium Hydroxide was added to the solution, where more ammonia was added to, again, make the solution clear again. To form a thin layer of silver, 1 drop of glucose was mixed with every 3 drops of silver solution. After the silver layer forms, electroplating can occur via the conductive seed layer.

3. Results

The first experimental setup, unfortunately, did not yield the desired results. Over 8 hours, a thin nickel layer plated the copper lead, but no substantial layers formed. Instead, nickel ions migrated to the plating site, but did not solidify. The mold did succeed in controlling the placement of the nickel ions, but no further control, such as constructing a conic shaped nickel, was acquired, and no noteworthy thickness changes were recorded. Figure 4 shows the outcome of the experiment to the copper lead with the RP mold placed on top of it.

Figure 4. Copper piece with small nickel plated region (outcome of experimental setup #1)

The second setup, with the circuit closed via seed layer, also failed expectations to electroplate. The solution, for several reasons, did not act as a seed layer on the rapid prototyped surface. A GaIn trail, meant to be a conductive pathway to the outer boundary of the tubing, became too thin or separated under the pressure of the rubber washer and clamps.

In a third experiment, a piece received a seeded layer, but a copper lead completed the circuit in the same fashion as Figure 2a. The resulting outcome was the same as the first setup with no layering in most cases. There was limited plating only on the copper strip's exposed region, with small amounts of plating visible on the bottom of the sloped region of the mold. Thus, the layer does conduct small amounts of electricity, although overpowered by the copper lead's high conductivity. The silver seed layer, however, did attract a significant amount of nickel wire. There was enough to electroplate the entire silver surface, but the process takes over 48 hours to complete. Figure 5 shows a successful silver seed layer plated with a significant layer of nickel.

Figure 5. Successful electrodeposition using a silver seed layer

There could be many reasons why the electroplating process failed in these experiments. In both cases, the nickel wire's outer layer oxidizes through the course of the electroplating. This oxidation brings the crucial flow of nickel ions to a halt. To eliminate this, a new nickel wire must replace the old one every few hours to avoid disrupting the process. Depending on the voltage applied and decline in voltage (if battery powered), the oxidation will occur at different rates, although most electroplating experiments indicate that complete oxidation occurs in roughly 5 hours.

Another possible way to improve the electrodeposition of nickel would be to integrate a conductive lead in the rapid prototyped model so that the seeded region would merely act as a conduit for electron flow, but still receive the benefits of being fully conductive. U.S. Patent 5547558 states that the electroplated surface contains an integrated copper foil array, possibly for easier circuit completion.

Third, the SLA technology creates a relatively smooth surface. The graphite particles used, being much larger than the optimal size (by more than four times), did not deposit well into the already shallow crevices. To route this, other methods less dependant on deposition should be evaluated.

4. Conclusion

Although the project encountered many technical problems, a successful method for electroplating rapid prototyped molds emerged. In general, for controlled and targeted electrodeposition to take place, a conductive seed layer of silver should be placed on the walls of the RP mold's surface. Without this, a concentration of ions builds up at the point of interest without fully electroplating. Silver seed layering performs well, but only with long periods of time to electroplate. Additionally, the use of power sources should route battery life failure. In the future, the silver electroplating method could be investigated further, such as measuring the slope or the electroplated layer and gauging voltage applied vs. electroplating time.

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