Manufacturing and Electroplating of Nanoengineered Polymers

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A polyethylene based polymer with metallic nanoparticles was recently developed as a nanoengineered polymer. The motivation for this project is the proposed use of these novel nanoengineered polymeric materials in many industrial and commercial applications. This necessitated the production of sheets using the nanoengineered polymer and electroplating selected areas using different metallic layers. The nanoengineered polymer resin provided by SABIC as beads of ~1 mm dia. was formed into sheets using compression molding. This research exploited selective electroplating methods to deposit nickel and copper layers of different thicknesses using pulsed electroplating techniques. These studies showed that higher duty cycle helped to improve the plated film properties. The quality of the electroplated nickel and copper films were examined using Scanning Electron Microscopy and Optical Microscopy methods, while the mechanical properties (e.g. Young’s Modulus, Hardness) of these films were analyzed using Nanoindentation. This paper describes the details of the manufacturing methods used for making the sheets of these novel nanoengineered polymers and further discusses the results of our studies on the electroplated copper and nickel films.

1. Introduction

The development of a nanoengineered polymer has opened up great potential for many new commercial and industrial applications. The polyethylene based material with metallic inclusions benefits from a wide variety of forming and manufacturing possibilities. The polymer resin ships from the manufacturer as 1 mm diameter polymeric beads. All subsequent forming operations were completed at Western Michigan University’s Plastics Lab. Several forming methods and parameters were examined to determine the most robust processing technique to produce the required substrates, without altering the semi-conductive nature of the polymer.

Industrial and commercial usage of this polymer benefits from the addition of an electrically conductive metallic coating. Successful application of a metallic coating lowers the resistance to negligible levels in select patterns atop the polymer substrate. Previous research into the electroplating of insulator and semi-conductive polymers has been met with limited success.

One method involves an electrode in contact with the substrate to be plated. This technique depends on the outward propagation of the deposited material originating at the contact point of the electrode with the substrate [1]. However, this method yields a slow rate of deposition and great effort must be used to control deposition to avoid the tendency of the film thickness to taper off as the distance from the electrode contact point increases.
Research conducted by Ghantasala and Sood aimed to electroplate on a selectively resistive (2–20 ohm-cm) silicon wafers without the need for a base film [2]. Their methodology consisted of ion implantation on the face of the silicon to induce selective seeding. In this case 19 keV Pd+ ions are implanted at various dosage levels. Electroplating was preformed to deposit permalloy on the substrate. This would demonstrate that continuous film occurred only in the regions where ion implantation was preformed [2]. The absence of any permalloy deposits in the regions without ion implantation indicate the importance of ions on the substrate surface and their purpose of inducing nucleation sites (eventually evolving into continuous plating). This clearly shows the importance of the nucleation process to occur on a semi-conductive substrate surface and the metallic ions on the surface.

There are numerous factors that alter the deposition and properties of an electroplated material. This research aims to focus on three important factors (material, current density, and duty cycle) with the goal of optimization given a set of parameters. Optimization is defined in this context as an electroplated coating with superior mechanical and electrical properties.

2. Experimental Procedure

2.1 Manufacturing of Nanoengineered Polymer Test Plaques

Elevated temperature extrusion was chosen as the primary method of forming for the samples, due to the ease of manufacturing and also the various output geometries that can be achieved. It was crucial during the forming stage that the parameters were selected such that the dispersion of the metallic inclusions in the polymer (that contribute to its semi-conductive nature) were not adversely effected [3][4].

The samples were produced in two stages. In the first stage the polymeric beads were feed into a 3.175 cm Killion Extruder with a coat-hanger type sheet die shown in Figure 1. The specimen was extruded as a continuous sheet which is 13 centimeters. Every 15 centimeters a cut was made to separate the sample into discrete units.

Figure 1: 3.175 cm Klein Extruder with a Coat-Hanger type Sheet Die
The sample sheet is then transferred to the compression stage, in an effort to provide a consistent surface finish. The sample plaques were formed in a P-20 Steel and Ampco 940 SiNiCrCu compression mold, which were placed into a 222,000 Newton Drake Compression Molding Press. During this compression process the sample is subjected to 133,500 Newtons of force for 60 seconds. The result is a sheet with a thickness of .7 mm. It is observed after the compression stage the ductility and resistance to fracture (compared to non-compression molded samples) had increased.

The surface finish of the sheet, post-compression molding was determined sufficient. However it was desired to explore other manufacturing possibilities in an effort to develop a robust process. Thus a rolling operation was examined to determine its validity as a forming operation, as well as its effect on the surface finish. As such the samples were fed from the extruder directly through a Killion Three-Roll Mill, Figure 2.

![Figure 2: Extrudate being fed into the 3-Roll Mill](image)

This process utilizing rolling compression of the sample greatly reduces the sample fabrication time as a continuous sheet is produced without the need for individual, discrete, compression stages. The resulting sheet samples are found to have a similar surface finish and thickness as those samples that were compression molded. To prepare the samples for electroplating 50 mm diameter circles were cut from the polymer sheets to create substrate wafers that could then fit within the wafer electroplating fixture. The samples were cleaned with acetone to remove any contamination from the forming process.

2.2 Electroplating of Nanoengineered Polymer

The electroplating was performed in a clean room environment. As it were desired to only deposit film on one side of the substrate only on a selected area, a special fixture was designed that allows for complete immersion of the substrate while exposing a selected portion of the substrate on the front side (where electroplating is required) to the electrolyte solution. The electrolyte solution was contained in a 1000 mL Pyrex beaker located on a hot plate, as shown in the set-up in Figure 3. A hot plate was used to maintain proper electrolyte temperature as...
monitored by a thermometer. Also presented in the figure is the anode (nickel or copper plates), as well as the sample jig that encases the nanoengineered polymer substrate.

![Image of Electroplating Setup]

**Figure 3: Electroplating Setup**

The current source used for electroplating was a Dynatronix MicroStar Pulse Precise Series DuPR10-5-1.5XR Pulse Power Supply, capable of providing 1.5 A peak current (.5 A continuous) at a maximum of 10 V output. A number of electroplated nickel and copper samples were prepared covering the range of parameters presented below:

- **Film Material:** Nickel, Copper
- **Current Density (mA/cm²):** 5, 10, 15
- **Duty Cycle (%):** 25, 50, 75, 100

Current density is calculated based on the area to be plated. The primary effect of current density is the rate at which the material is deposited onto the cathode. Thus for a higher current density, a given amount of deposit is achieved in a shorter period of time. The increase in current density is brought on by an increase in the average current (given a constant plating area). However, this can result in adverse effects on the microstructure of the films.

The duty cycle is the ratio of the ON Pulse time to the ON + OFF Pulse time, with 100% duty cycle corresponding to Direct Current (DC) plating. Pulse plating covers the range of duty cycles from greater than 0% to less than 100%. The result was a periodic interruption of current flow. This interruption allowed for a dispersion of a negatively charged layer that forms around the cathode while current was applied. This layer can inhibit ion mobility, thus decreasing the process efficiency [5]. Early work by W. Kleinekathofer indicated pulse plating (as compared to DC) has a finer micro-structure and a reduced porosity [6]. One of the requirements of pulse plating is the need for higher peak current to maintain a constant cathode current density. For low duty cycles this can produce a large spike in the current, which can lead to “burning” of the deposited material [7]. For example if a 100 mA average current is desired with a 10% duty cycle operating at 1 Hz; the result would be a 1 A current.
flow for .1 sec followed by a .9 sec pause with no current flow.

2.3 Characterization:

The electroplated copper and nickel films were examined in a Scanning Electron Microscope (Philips XL30-FEG, USA). This system is capable of providing a resolution of 3.5 nm at its maximum voltage of 30 kV. Further, instrumented indentation was employed to measure the mechanical properties of the deposited films using a CSM Nano-Indentation Tester having relevant software.

3. Results and Discussion

3.1 Manufacturing of Nanoengineered Polymer

One of the most crucial aspects of the polymer sheet forming process is to preserve the nature and distribution of the metallic nanoparticles within the host polymer matrix. As the relative distribution of the metallic nanoparticles can greatly affect the electrical conductivity of the polymer, process optimization was performed during this step. Results from the initial forming operations determined that the density of the inclusions within the polymer had decreased after extrusion. This yielded sheets with higher resistance. To remedy this situation it was determined the screen pack within the extruder (which aids in the melting process by increasing the back pressure) had to be removed, as it was interfering with the metallic inclusions. Removal of the pack filter was successful in restoring the extrudates resistance to pre-forming levels.

The manufacturing of the polymer samples into substrates can be achieved through a variety of methods, each with their own set of optimization parameters and results. The elevated temperature extrusion chosen in this analysis is no different. One of the key parameters concerning this forming method is the temperature at which the polymeric beads were melted. Initial tests were conducted at a melt temperature of 200°C. At this temperature the extrudate featured “tearing” at the surface of the polymer, indicating of a melting temperature that is too low. As such the melt temperature was increased to 215 and eventually to 225°C to eliminate the “tearing” effect of the polymer.

Following the extrusion, the compression molding process utilized to form the plaques was optimized to produce an acceptable surface finish. This included a minimum compression time of 60 sec to allow for the polymer to cool. Additionally the compressive pressure was adjusted between 30,000 and 44,000 psi in which it was determined the optimal value is 30,000 psi. This process proved sufficient; however the requirement of the sheets to be cut into discrete units for the press increases the manufacturing time and limits large scale viability.

The rolling operation chosen to replace the press allows for a greater rate of production, as a continuous sheet could be generated with no interruptions to the process flow. Optimization of this operation has been carefully controlled to ensure the material output rate from the extruder matched the speed at which the rollers accept the material. Otherwise stretching and ripping can occur resulting in failure of the material. The rate of the rollers is adjusted to match the extrudate velocity. The extrudate velocity is a function, among other parameters, of the die
pressure as well as temperature. It was determined at a die pressure of 22 MPa and temperature of 245°C the rollers operated at their maximum rotational velocity of 75.1 RPM. To decrease the rotation velocity of the rollers the die pressure is decreased to 11-12.5 MPa at a temperature of 240°C which resulted in a roller speed of 65 RPM, a stable value.

3.2 Electroplating of Nanoengineered Polymer

SEM images of the copper and nickel electroplated samples prepared at different duty cycles 25%, 50%, 75% and 100% were compared as in Figure 4. To provide for an accurate comparison the current density was kept constant at 10 mA/cm². All these samples were electroplated for duration of 90 min each.

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<th>Duty Cycle / Material</th>
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<th>Nickel</th>
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<td>100%</td>
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Figure 4: SEM pictures of copper and nickel films deposited at duty cycles 25%, 50%, 75% and 100% respectively (50x)

From the SEM images presented in Figure 4 it is clearly seen that the nickel films appear...
relatively porous compared to the copper films at all duty cycles. Throughout every duty cycle the copper film presents a greater level of homogeneity with fewer discrepancies. It can also be observed in both cases, the porosity of the deposited films decreased with increasing duty cycle.

In addition to the film topography, the microstructure and size of the individual grains in the deposited Nickel and Copper films were also determined from the SEM analysis, in order to understand the nucleation process. Figure 5 presents the SEM images of these samples at a higher magnification level of 5000X.

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Figure 5: SEM pictures of copper and nickel films deposited at duty cycles 25%, 50%, 75% and 100% respectively (5000x)
These SEM pictures in Figure 5 clearly show a large amount of variation in the microstructure and associated grain size between the copper and nickel films. While the copper films showed a distinct granularity, the nickel films appear smooth and quite reflective topography. At a 25% duty cycle, the copper film displays an average grain size of the order 3 to 5 µm. The copper films deposited at a duty cycle of 50% exhibited an average grain size of 1 to 3 µm. As the duty cycle further increased to 75%, this trend continues with the grain size decreased to .5 to 2 µm range. Interestingly, relatively smooth sub-µm grains were observed in copper films electroplated using DC constant current (100% duty cycle). In contrast, nickel films deposited using pulse plating at different duty cycles appear smooth without any granular features. However, the DC plated (100% duty cycle) nickel films seem relatively rough compared to others.

As microstructural variation with grains of different sizes known to influence the physical and mechanical properties of thin films, these changes will be correlated with the film properties. Smaller grain sizes yield significant advantages in terms of wear resistance [8]. Additionally, the decrease in grain size leads to an increase in the density of grain boundaries which in turn improves the fracture mechanics of the material.

These films were analyzed using nanoindentation technique also for Young’s Modulus and Hardness properties. Correlating the nanoindentation results to the SEM data shows that the relatively larger grain structures of the Copper deposits are related to a higher Young’s Modulus and lower Hardness when compared to the Nickel deposits. The Nickel deposits with the smaller, featureless, grains correspond to a relatively higher hardness. Consistent with mechanical theory in which smaller grains (which yields an increase in grain boundary density) have improved mechanical properties such as wear properties, fracture resistance, as well as the observed Hardness. This trend continues within the Copper samples wherein it is found an increase in duty cycle (and thus a decrease in grain size) results in a higher Hardness value.

Examination of these plots indicates that the data conforms well to a linear trend line. It shows that Young’s Modulus and hardness are both linear functions of current density as well as duty cycle. This trend appears as a positive slope for both copper and nickel. An increase in duty cycle and/or current density correlates to a direct increase in the samples Young’s Modulus and hardness, an important determination in the characterization of the thin metallic films. Additionally, copper exhibits a higher Young’s Modulus when compared to nickel for each duty cycle/current density combinations. This was contrary to the bulk properties relationship of the two materials (bulk copper Young’s Modulus = 110 GPa, bulk nickel Young’s Modulus = 200 GPa)[9], indicative of a scaling factor that alters the materials mechanical properties at the micro-scale. From the SEM results the grain size is roughly 3-5 microns. Thus the grain size of bulk copper can be assumed to be in this range. The bulk value for the Young’s Modulus of Nickel was not observed during the course of this research. The nickel films in general exhibit a higher hardness when compared to the copper films, consistent with the relationship of the bulk material mechanical properties.
Conclusions

The manufacturing of the polymer resin from beads into test plaques was demonstrated in this paper using a combination of forming methods. The chosen process for this research involved elevated temperature extrusion coupled initially with compression molding, later replaced by a rolling operation. It was determined both post extrusion operations resulted in a similar surface finish of the sample; however the increase in throughput of the rolling operation was a clear advantage. Optimization efforts of the manufacturing process resulted in samples with unaffected electrical conductance properties in a choice of geometries. Copper and Nickel electroplated samples were prepared at different duty cycles and current densities. The analysis of the copper and nickel samples showed that copper films were much more granular with the grain size varying in the range 0.5 µm to 5 µm, whereas Nickel films were relatively smooth. It was determined that within a given material, mechanical properties rely on the plating current density and duty cycle. An increase in either factor results in improvement of mechanical properties. With respect to the individual material results, copper was found to have a higher Young’s Modulus (for equivalent deposition parameters) while nickel exhibited a higher Hardness (for equivalent deposition parameters).

Bibliography


