Formation of Highly Electrically Conductive Surface-Silvered Polyimide Films Under Exceptionally Mild Conditions

Tyler Stukenbroeker
College of William and Mary

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Formation of Highly Electrically Conductive Surface-Silvered Polyimide Films Under Exceptionally Mild Conditions

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelors of Science in Chemistry from The College of William and Mary

by

Tyler Stukenbroeker

Accepted for (Honors, High Honors, Highest Honors)

David Thompson, Director

Christopher Abelt

Gary Rice

Clay Clemens

Williamsburg, VA
May 5, 2010
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INTRODUCTION

Background of Polyimide Synthesis and Characterization

Group research on polyimides began from efforts at NASA’s Langley Research Center. Polyimides garner high interest there for the same reason they do all over the world: excellent mechanical properties, low dielectric constant, high breakdown voltage, good processability, wear resistance, radiation resistance, inertness to solvents, good adhesion properties, low thermal expansion, good long term stability, and high fire resistance, among other properties. High molecular weight polyimides were first produced in the late 1950’s by DuPont. These discoveries were patented in 1959 and were quickly utilized by electronics companies and the Department of Defense. Today, DuPont continues to produce polyimides commercially under the brand name Kapton. Kapton was used extensively for the Apollo 11 program and continues to find use in space, aeronautics, clothing and electronics applications. It can withstand temperatures greater than 400°C. General Electric marketed a competing polyimide, Ultem, until it was acquired by Saudi Basic Industries Corporation in 2007. Ultem is used for many of the same applications.

There are numerous ways to synthesize a polyimide. The approach used in this study to achieve polyimide synthesis is a two-step method (Figure 1). First, a poly(amic acid) is synthesized. This reaction takes place readily between diamines and dianhydrides in polar aprotic solvents. The amino groups attack one of the carbonyl groups of the anhydride, opening the ring. The condensation reaction is exothermic. Even at room temperatures, it is not difficult to attain high molecular weight polymers.
Figure 1: The two step polymerization scheme for creating the 6FDA/0.5 4,4'-ODA-0.5 DABA polyimide. Note that the final product is a random copolymer, so the monomers may not alternate as suggested by the drawing. The pendant carboxylic acid has been circled in green.
Various cations can be coordinated with the free acid group created in the ring opening. Early group studies drew on techniques pioneered by Abadie and Akamatsu.\textsuperscript{24-28} A poly(amic acid) was silvered by dissolving and sometimes coordinating the silver cation within a polymer film before reducing it to metallic silver. Successful group trials led to the polyimide metallization effort of which this study is a part.

The most common way to close the opened ring of the amic acid is via thermal imidization. This process is most readily carried out on polymers in the solid state: those that have been cast and dried of solvent. The temperature required for imidization varies based on residual solvent and other factors but is typically 300\textdegree C.\textsuperscript{3} This study used a chemical route to the polyimide instead. Here, a dianhydride and an amine are added to the solvent. The amine, such as pyridine, serves to deprotonate the poly(amic acid). An anhydride group is formed on the polymer. This reactive intermediate rearranges to reform the polyimide ring and loses a water molecule. This process successfully imidizes the polymer under gentle heating. The polyimide must then be removed from the solvent and pyridine via drying or precipitation. The latter method is especially attractive due to how readily the polymer precipitates into cold water.

Much of the NASA research centered on fluorinated polyimides. Fluorination of these molecules is known to modify the optical properties, often providing transparent polymers.\textsuperscript{4} There is considerable interest in these types of fluorinated polyimides for solar cell applications. The fluorinated dianhydride monomer used in the LARC-CP1 and LARC-CP2 polymers is 6FDA (Figure 2). This molecule was also chosen for this study due to enhanced optical properties without sacrificing many of the high performance structural and thermal properties of the polyimide. For instance, in the
Figure 2: Structures for two NASA polymers and the copolymer used in this study. Additionally, the silver(I) HFA complex is shown with resonance.
event that silver metallized underneath a thin layer of polymer molecules, the transparent fluorinated polyimide would have a minimal effect on the reflectivity compared with a non-fluorinated variety.

Casting the films can be carried out a number of different ways. Commercial polymers are produced with an extruder. This device is usually fed pellets of polymer, which is subjected to high heat and pressure. The polymer resin is then forced through a die to mold it and then cooled in a water bath. This study did not have an extruder on-hand to use. Therefore, casting was limited to solvent evaporation methods. The dried, powdered polyimide is mixed with solvent at a given ratio. The polymers used in this study were especially soluble relative to other polyimides, but there was still difficulty in dissolving at greater than 15% by weight fractions in the solvent. Once the polyimide was dissolved, the solvent is poured onto a substrate, often a glass plate, and quickly leveled to a given thickness with an applicator blade. Moisture in the air will cause the polymer to precipitate out almost immediately, so the film is left in a low humidity environment to allow the thin layer of solvent to evaporate.

Characterization of polyimides can be carried out via a number of optical techniques, particularly FTIR. From the magnitude of the C-N stretch one can estimate the percent of the polymer that has been imidized. X-ray diffraction may also provide useful information regarding orientation and crystallinity. Finally, a number of polymer tests can characterize the structural and thermal properties of the polyimide. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermogravimetric analysis (TGA) can all provide more information about the polyimide on a macroscopic level. These techniques are all relevant to bulk polymer
characterization. A number of other techniques are available for surface characterization including electron spectroscopies, vibration spectroscopies, microscopy, and surface energy measurement.

For TGA analysis, the weight of the polymer is measured as temperature is ramped up to some extremely high value, past the point where the polymer has disintegrated. TGA is a useful indicator of thermal stability because polyimides are not often used in load-bearing structural applications. Especially in high temperature applications, the polymer is used exclusively for protecting other structural components. Therefore, percent of weight retained is a good estimation of how well the polyimide will perform. TGA analysis reveals that many polyimides maintain the majority of their weight at temperatures greater than 500°C.

A number of factors can increase polyimide instability at high temperatures. Degradation occurs in the polyimide ring. At high temperatures the ring may open again to create the poly(amic acid) (which is quickly decarboxylated), or a six membered ring containing adjacent nitrogen atoms. Rearrangements may occur, creating less stable structures such as isoimides or imidines. The presence of water also helps break down the polymer. Degradation usually begins at “weak links” in the polymer such as uncyclized bonds. The presence of trace metals or residual solvent is known to be detrimental to stability.

Unlike more active metals such as aluminum or chromium, vapor deposited silver does not adhere to plastic surfaces. Yet there are numerous applications for silvered polymer films ranging from electronics to art and satellites to medicine. For example, silver has been shown to possess antimicrobial properties. Silver ions are thought to
inhibit bacterial enzymes and bind to DNA. Metallizing polymer surfaces such as catheter tubes could mean fewer infections. NASA is interested in silver metallized films for a variety of space applications. Antennae could be created that would be much lighter than a solid metal version. This would be a significant benefit for reducing the payload of satellites and extra-planetary crafts. Other, more exotic, space applications such as solar sails have also drawn interest. The simplest way to achieve such films is to use physical vapor deposition of chromium. This creates a surface onto which silver will adhere if it is vapor deposited. This process is both time consuming and costly. A direct route to a permanently adhered silver surface is necessary.

This can be accomplished by doping the dissolved polymer with silver(I) ions, casting the polymer, and then reducing the ions via heat. This technique successfully creates a reflective and conductive surface that is permanently adhered. Though this eliminates the chromium step, films must be heated at approximately 300°C for several hours. This may lead to undesirable effects. For instance, most electronic microchip components could not tolerate such conditions. Furthermore, it is possible it could have negative structural implications for the polymer substrate. Polymers not designed to withstand high heats will undergo thermal degradation, weakening the molecular backbone and causing macroscopic cracks.

Therefore, earlier group work had focused on formulating a chemical reduction route that could be carried out at room temperature. This study stems from that effort. Past work used a trifluoromethanesulfonate-silver(I) complex to introduce silver ions. Published work using this compound is reprinted here in Appendix A. Unfortunately, excess triflate ligand is extremely acidic, and threatens the long-term integrity of the
polyimide. Many films doped with these complexes showed significant degradation evident through macroscopic cracking after a period of one to two weeks. This study relied on silver(I)-hexafluoroacetylacetate (silver(I)-HFA), a less corrosive complex, to achieve the same result (Figure 3). However, swapping the silver complex resulted in a number of alterations to the final product that became especially evident with electron microscopy. Essentially the new complex required a reconfiguration of the reduction process in order to optimize the conductivity and reflectivity of the final product. Also, a number of other applications for silvered polyimide films were investigated.

**EXPERIMENTAL SECTION**

*Experimental Materials:* The following chemicals were purchased from Sigma-Aldrich (Milwaukee, WI) and used without further purifications: N,N-Dimethylacetamide, anhydrous, 99.8%; 1-Methyl-2-pyrrolidinone, anhydrous, 99.5%; Silver(I) oxide, 99%; Silver Acetate, 99.99%; Sodium citrate dihydrate, 99+%, Azodicarbonamide, 97%; Hydrazine monohydrate, reagent grade, 98%; 1,1,1,5,5,5-Hexafluoro-2,4-pentanediione, 98%, Hydroxylamine, 50 wt. % solution in water; 3,5-Diaminobenzoic acid, 98%. The following chemicals were purchased from Fisher Scientific (Fair Lawn, NJ) and used without further purifications: Silver Nitrate, Certified ACS; Ammonium Hydroxide, Certified ACS. The following chemicals were purchased from ChrisKev Company, Inc (Leawood, KS): 4,4'-diphenyl ether or oxydianiline (ODA). The following chemicals were purchased from Hoechst (Germany): 2,2'-Bis (3,4-Dicarboxyphenyl) Hexafluoropropane Dianhydride. The following chemicals were purchased from Transene Company Inc. (Danvers, MA): Silver Etchant Type TFS.
Figure 3: Drawings of the two ligands used to complex the silver. On the left are triflic acid and the silver(I) triflate complex. On the right are hexafluoroacetylacetone and its silver(I) complex.
The first step was recrystallizing the DABA monomer. Polymerization was carried out in a round bottom flask fitted with a stirring attachment and kept under a nitrogen atmosphere. The two diamine monomers were added as solids, and then DMAc was added with stirring. Finally the 6FDA dianhydride was added with more DMAc and the entire mixture was stirred at room temperature for one day. This created a polyamic acid. Chemical imidization was carried out by adding acetic anhydride and pyridine. This was accompanied by gentle heating. The polyimide was then dripped into distilled water to precipitate it. The final product was filtered and dried in a vacuum oven.

To synthesize the doped polymer silver from a silver salt, either silver oxide or silver acetate was dissolved in dimethylacetamide (DMAc). The HFAH, a volatile liquid at room temperature, was added to the solvent a 1.1:1 ratio to the silver(I). The excess ligand ensured that all the silver was complexed. The mixture was stirred for five minutes or until all visible traces of the silver salt were gone to ensure the complex had formed. The copolymer described above was then dissolved into the solvent, yielding a doped, dissolved polymer mix. Up to 15% by weight solid polyimide could be dissolved into DMAc. After 15 minutes or more of stirring, the solution was homogenous. The mixture was cast onto glass slides at a thickness of 0.45mm and allowed to dry for 24 hours in a low humidity (<5%), high flow (95 SCFM) dry box. Studies showed that this 24-hour period was sufficient to remove 96.7% of the DMAc (Figure 4). This study was carried out by carefully weighing glass slides with the cast polymer directly after they had been cast and at regular intervals thereafter. After factoring out the weight of the slide and solids in the solvent, it was possible to determine the rate of evaporation.
**Figure 4:** Graph of DMAc solvent evaporated over time since polymer film casting.

The low boiling point of DMAc (165°C) allows it to readily evaporate from thin films at room temperature. After 24 hours only 3.3% of the original DMAc remained in the film; approximately 16% of the dried film was solvent.
The doped polymer films generally adhered very well to the glass slides and only released from them in a water bath.

The final step was chemical reduction. Solutions of a reducing agent were prepared. Hydrazine and hydroxylamine, both sold as liquids mixed with water, were diluted to 1M solutions with deionized water. Ammonia was also diluted to 1M. The appropriate quantities of a reducing agent and of ammonia were added to a 3 cm jar along with deionized water to achieve the proper concentrations of each. The jar was capped and shaken vigorously by hand for 10 seconds to ensure mixing. The reducing agent was then applied via Pasteur pipette to the surface of the film in approximately 1 mL portions. This was allowed to sit in air at room temperature for the desired number of minutes. Reducing agent was removed initially by blotting with Kim-wipes and then by rinsing the film under deionized water for 15 seconds.

*Characterization of the films was performed with the following instruments and techniques:* TGA analysis was performed using a TA Instruments Q500 TGA. Resistivity measurements were taken with a Tenma 72-7755 multimeter with the probes 1cm apart. Readings were taken three times at different locations, and more if they differed by more than 0.2 ohms. The average value was taken as the two point resistivity. Reflectivity measurements were taken on Perkin-Elmer Lambda 35 Spectrometer standardized against a Perkin-Elmer polished aluminum mirror with a reflectivity coefficient of 0.92. Microscopy was performed using a Hitachi S-4700 field emission instrument (SEM) and a JEOL TEM instrument located at Jefferson National Laboratory and operated by Old Dominion University. The latter instrument is capable of 0.1nm
resolution. TEM samples were sliced by an ultramicrotome and placed into a polymer resin. Once the resin dried the samples were prepped for analysis.

*Room Temperature Metallization Procedure*

The room temperature method for reducing the silver(I) doped polyimide films relies on chemical rather than thermal reduction. An aqueous reducing agent is placed on the surface of the film via pipette allowing it to reduce the silver(I) ions in the uppermost layer of the film. This would seem an even simpler technique than thermal reduction. However, unlike heat, the aqueous chemicals cannot penetrate into the bulk of the polymer. Only silver ions at the surface may be reduced. The majority of the ions, located in the bulk of the polymer, must migrate to the surface of the film in order to be reduced. Potentially, this could lead to a thicker silver layer on the surface, increasing conductivity and reflectivity. However, it also requires ion mobility, a problem that was solved by creating a new copolymer. The starting point was a high performance NASA-inspired polyimide 6FDA-ODA. Half of the oxydianaline (ODA) monomers were replaced with a 3,5-diaminobenzoic acid (DABA) group. The product was a random copolymer 6FDA/0.5 DABA-0.5 ODA. The key aspect of this new polymer is the pendant carboxylic acid chain. This lent more ionic character to the polymer environment, making it easier for ions to migrate. The thermal stability and integrity of this polymer was tested with thermogravimetric analysis (TGA). The copolymer degraded just below 600°C (Figure 5).
Figure 5: TGA analysis of the undoped copolymer and the metallized HFA film. Note the initial weight loss due to decarboxylation of the pendant carboxylic acid group.
Both hydrazine and hydroxylamine were used effectively as reducing agents. Sodium borohydride was also used initially, but was abandoned due to the ease of preparing solutions with the other two as well as unidentified surface alterations that appeared with the sodium borohydride, most likely byproducts of the reduction. Both hydrazine and hydroxylamine break down to form nitrogen gas, hydrogen ions, free electrons for reduction, and in the case of hydroxylamine, water. Sodium borohydride, however, leaves boric acid as a byproduct. Note that the protons formed in the reduction process are recaptured by the ligand that was bound to the silver. Therefore, a weak conjugate base of a strong acid like triflic acid leaves free protons in the polymer to react and cause damage. HFA-H, with a pKₐ of only 5.3, recaptures some of the hydrogen ions.

In comparison with hydroxylamine, hydrazine donates four electrons per molecule, whereas hydroxylamine only donates one. Therefore, when comparing “equivalent” concentrations of the two reducing agents, the actual concentration of hydrazine is only one-fourth of hydroxylamine. Though hydrazine has a weaker reduction potential than hydroxylamine (-0.23V vs. -2.22V) both are strong enough to reduce silver (0.80V). Hydroxylamine is a stronger reducing agent, but hydrazine is more efficient.

The strength of the conjugate base is important. Note that films created with soluble silver salts such as silver nitrate form doped films that are readily metallized. In fact, under identical conditions these films outperform both of the silver complexes in conductivity, not to mention advantages of cheaper starting products and a simpler synthesis. However, the nitrate counter ion is unable to capture any of the free hydrogen
ions, posing a threat to the long term stability of the polymer. Furthermore, the oxidizing properties of nitrate could further damage the polymer.

With the above elements in place, metallization of the silver(I)-HFA films will occur. However, it proceeds at an exceptionally slow rate, often taking more than ten minutes to form a reflective surface and sometimes never forming a surface at all. Most often, transparency of the surface was used as an on the fly indicator of how rapidly the metallization was proceeding. If it was possible to see the motion of shapes or text through the film, the metallization had not proceeded sufficiently. Ammonia was needed to promote the reduction process by accelerating migration of the silver ions. The hypothesis from earlier work was that silver migration to the surface was enhanced through two routes. First, the coupling of ammonia with the pendant acid chains gave the polymer ionic character which was more conducive to silver ion migration. Second, the ammonia formed a new complex with the silver ions, diamminesilver(I), which served as a protecting group for the migrating silver. Once the silver reached the surface of the film, it was reduced. This hypothesis was supported by both the demonstrated acceleration of silver formation in the presence of ammonia as well as by microscopy, described below. An additional route of increasing the efficiency of the process was combining the ammonia and reducing agent prior to application, and then applying the mixture to the film.

While mixing ammonia with the reducing agent greatly accelerated the metallization process, it required a freshly mixed solution. After approximately 24 hours, a mix began to lose effectiveness, regardless of the reducing agent used. Eventually, this
was traced not to the reducing agent, but to the ammonia itself. Evidently, the ammonia was evaporating into the air if care was not taken to properly seal the mixture.

RESULTS AND DISCUSSION

_Evaluating the Films and Conductivity Discussion_

Films that were prepared with the silver(I)-HFA complex matched or exceeded the conductivity and reflectivity of films with the triflate complex studied by Davis, et al. Additionally, the cracking phenomenon with the triflate films was not observed. Films that had been doped were treated with N₂H₄ and NH₂OH six months later with no reduction of conductivity or reflectivity. Although the doped polymer degraded at a temperature nearly 200°C cooler than the undoped copolymer in TGA analysis, it still showed good performance. Also, measuring resistance with a two point probe was perhaps not the best method of determining resistance on a metal sheet. In previous work a four point probe to get was used surface resistivity measurements, which consists of four tungsten electrodes placed in a line on the surface. Current is run through between the outer two electrodes, and the voltage is measured by the two inner electrodes. Surface resistivity is the measured voltage required to maintain a given current divided by that current. The primary goal of this setup is to prevent resistance between the probes and the surface from interfering with the measurement. Additionally, the surface resistivity measurements can be scaled by a constant related to the geometry of the surface to account for the fact that the current can take a number of different routes from one electrode to another, rather than a straight line as is the case for a wire. When
this is taken into account, the measurement is known as sheet resistivity and uses units of ohms per square. The surface resistance measurements from a four point probe were found to correlate very well with the readings from the two point probe (Figure 6). The natural logarithm of the resistance was used, since resistance is not a linear scale. Also, those films with resistivities above $e^2$ were excluded. As shown, the two probes correspond quite well, with an $R^2$ value of 0.88. For this reason, and due to the ease of taking two point readings, all resistance measurements listed from this point forward were from a two point probe.

In addition to promising conductivity, the films displayed good reflectivity (Figure 7). In addition to specular reflectivity measurements, each film was given a qualitative reflectivity score of 1-5 based on a visual inspection. While imprecise, it was enough to show that conductivity and resistivity were often not related. Ultimately, the primary concern became minimizing the resistivity, since most applications relied heavily on the conductivity of films.

Statistical Treatment and Development of a Model

To accomplish resistivity minimization, the entire process had to be optimized for the HFA silver complex films. Initially five variables were tested: (1) silver source (silver acetate or silver oxide,) (2) silver concentration (4, 6, or 8 wt. %) (3) reducing agent
**Figure 6:** Experimental relationship between two point resistivity measurements taken with a two-point probe and surface resistivity measured with a four-point probe. Values outside the range of the plot were excluded from the analysis.
Figure 7: Pictures of the metallized films. The upper image is a reflection of the camera, and the lower image shows the glass slides on which the polymer is often cast.
(hydrazine or hydroxylamine) (4) reducing agent and ammonia concentration (.5/.5M, .05/.05M, or .005/.005M), and (5) application time (2, 4, or 6 minutes). These were all varied individually in order to determine the most effective and the most efficient path to metallization (Figure 8).

The results of these tests were subsequently analyzed by statistical software, Stata (StataCorp), to determine the contribution of each variable and the significance of that contribution. In order to analyze all five variables simultaneously, both silver source and reducing agent were assigned dummy variables (silver acetate=0, silver oxide=1; hydrazine=0, hydroxylamine=1). The concentration of the reducing agent was assigned a value of 1, 2 or 3. The decision to use these dummy values rather than the actual molarities (which varied by factors of ten) was made based on observed correlations. Had the actual molarities been used, the degree of metallization afforded by the smallest molarity would have been overstated. Finally, the dependent variable, resistance, was also not a linear scale. Based on observation, it is clear that the resistance does not vary linearly with any of these factors. For example, with more silver added, the resistance will slowly fall, until there is not enough silver to coat the entire surface, at which point resistance will increase sharply. The best way to account for this in the model is to regress the independent variables against the natural logarithm of resistance. This is by no means perfect. Even after taking the natural logarithm, there are still a few exceptionally high values that would skew the rest of the data. This implies that an exponential model is not accurate at higher resistances. More advanced statistical methods would be needed to account for resistances that are orders of magnitude higher than the others. For this study, the goal was simply to get a model for the films that
Figure 8: Graphs of the effect of five different parameters on film conductivity. Note that each graph assumes that the parameter associated with it is responsible for all variation in resistance. See figures 9 and 10 for the regression models.
exhibit good conductivity. Therefore, it was acceptable to remove this higher resistance data points as outliers from the regression. The decision to drop or keep the higher values was made using Chauvenet's criterion. This model simply excludes data points if, according to a normal distribution, there is less than a 50% chance that they would occur. Mathematically, this means calculating the mean and standard deviation then finding the number of standard deviations the point in question is from the mean. The probability beyond that point under a normal curve is multiplied by the number of data points. If that value is less than 0.5, the point is dropped and the process is repeated. Using this criterion, the upper seven of 58 measurable resistances were excluded. These included values of 9 ohms and higher. While these exclusions limit the range over which the model can be applied, they help increase the normal distribution of resistance logarithms and lead to a more accurate model.

Once the data was prepared, a regression of the logarithms of the resistances against the five parameters that were varied was generated with Stata (Figure 9). Before examining the coefficients, it is important to look at the p-values for each variable. These p-values can be interpreted as the chance that the variable has no impact on the dependent variable. Thus, higher values indicate less confidence in the coefficient assigned to that variable, and values near one suggest the variable should be discarded entirely. The source of the silver had a p-value near one, so it may be ignored. The reducing agent had a p-value near 0.5, so it is highly doubtful. There was an 8% chance the time the reducing agent was applied was insignificant, and both reducing agent concentration and silver concentration were highly correlated to the independent variable. To interpret the coefficients, one must remember the regression was run against the natural logarithm of
Figure 9: Output from Stata statistical software. The variables listed, starting with
ln_resist, are the natural logarithm of the resistance, the initial source of the silver ion
(0=AgOAc, 1=Ag$_2$O), the weight percent of silver relative to the polyimide, the time the
reducing agent was applied (minutes), the reducing agent (0=N$_2$H$_4$, 1=NH$_2$OH), the
concentration of reducing agent (1, 2, or 3, with each step up being an order of magnitude
more concentrated) and finally a constant. The calculated model for predicting the two-
point resistance of highly conductive, HFA films:

$$\ln(\text{resistance})=0.0087*\text{ag}_\text{source} - 0.0935*\text{ag}_\text{percent} - 0.0611*\text{red}_\text{time}$$
$$+ 0.0653*\text{red}_\text{agent} - 0.6371 \text{ red}_\text{conc} + 3.006$$

However, the model can be simplified by dropping variables with p-values greater than
0.05:

$$\ln(\text{resistance})=-0.0935*\text{ag}_\text{percent} - 0.6371 \text{ red}_\text{conc} + 3.006$$
the resistance, so the relationship between the variables and resistance is not linear. In fact, a mathematical examination shows that a one unit change in a variable with coefficient x will change the predicted resistance by a factor of $e^x$. Therefore, the model predicts that using hydroxylamine instead of hydrazine will increase the resistance by $e^{0.65} = 1.07$ ohms, if the variable is relevant. An extra minute of applying the reducing agent increases the resistance by 0.94, or in other words the resistance decreases 6% for every minute the reducing agent is applied (Figure 10). Increasing the reducing agent concentration by a factor of ten decreases resistance by 48%. Increasing the wt. % of silver by one percent decreases resistance by 9%. Overall this model gave an $R^2$ value of 61%.

With these results in mind, a standard set of parameters for the reduction technique was established. Given their importance in creating a conductive surface, the maximum experimental concentrations of reducing agent and silver were used. Silver oxide was chosen as a silver source because it is cheaper. Hydrazine was given the edge over hydroxylamine and four minutes was chosen as the standard application time for the reducing agent.

Further Evaluation: SEM and TEM Microscopy

Having optimized the five parameters, the HFA films were analyzed by electron microscopy in hopes of learning about the mechanism of metallization. The conductive nature of the films was sufficient in most cases to allow for SEM analysis without sputter coating. The electron microscopy revealed dramatically different metallized surfaces
<table>
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<th>Parameter</th>
<th>Coefficient</th>
<th>p-value</th>
<th>Conclusion</th>
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<tr>
<td>Silver source</td>
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<td>.92</td>
<td>Whether silver is obtained from silver nitrate or silver acetate, conductivity is not effected</td>
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<td>Concentration of silver (wt. %)</td>
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<td>.00</td>
<td>Every time concentration of silver is increased by 1 wt. %, the resistance decreases 9%</td>
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<tr>
<td>Reducing agent application time</td>
<td>-.061</td>
<td>.08</td>
<td>Every extra minute the reducing agent is applied, the conductivity decreases 6%</td>
</tr>
<tr>
<td>Reducing agent</td>
<td>.065</td>
<td>.47</td>
<td>Whether hydrazine or hydroxylamine is used, conductivity is likely not affected</td>
</tr>
<tr>
<td>Concentration of Reducing Agent</td>
<td>-.637</td>
<td>.00</td>
<td>Increasing the reducing agent concentration by a factor of ten decreases resistance by 48%</td>
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</tbody>
</table>

**Figure 10:** Table summarizing conclusions of regression. When compared to the pre-regression relationships in Figure 8, it is clear that the variables are very interdependent.
between films of the two silver complexes (Figure 11). Where the triflate films had broad, dendritic growth, the silver(I)-HFA films showed many different nucleation sites. This surprising variation showed that there was a significant ligand effect. Despite the fact that the silver was no longer complexed, it still appeared that the ligands were impacting the final metallization step.

To obtain further analysis and a depth profile, the films were analyzed by TEM. The TEM instrument uses an electron beam, like an SEM, but places the detector on the opposite side of the sample. The thin cross section of sample allows some electrons to penetrate through to the other side and produce an image of the sample. In our case, silver metal blocked the beam but the polymer, including silver ions, allowed some electrons to pass through.

Surprisingly, the thickness of the silver surface was approximately 100 nm (Figure 12). This is only a quarter of similar silver thickness with the triflate films. It appeared that much of the silver from the HFA samples was “missing.” The bulk of the film was examined to try and locate silver that had been reduced and subsequently trapped within the bulk of the film. This effect was observed in some of the triflate films. However, there was little to no silver metal in the bulk. It is possible that the silver ions in the bulk are being reduced, but are too small to be seen. This is unlikely, however, given the surface effects of silver clumping into nanoparticles. Additionally, the resolution of the instrument approaches that necessary to make out atomic lattices, thus making it unlikely that particles were missed. More likely, the silver was too far from the surface to migrate and was never reduced.
Figure 11: Comparison of SEM micrographs. All scale bars are 1000 nm. The left images are from earlier work with triflate films, those on the right are HFA films. Note the difference in surface texture and the number of nucleation sites present in the HFA films. The triflate micrographs were collected by Luke Davis and are presented here with permission.
Figure 12: Comparison of TEM micrographs. Note that the scale bars are not equal between images. The left images are from earlier work with triflate films, those on the right are HFA films. The black areas are reduced silver and the darker gray side is polyimide. Note the presence of reduced silver in the bulk of the triflate films. Also note that the triflate films are nearly four times thicker than the HFA ones, despite containing less total silver. The triflate micrographs were collected by Luke Davis and are presented here with permission.
Further structural features were observed with the TEM. Below the large, clumpy surface layer are smaller silver particles. The presence of these particles is unique to the HFA films. As noted earlier, surface nanoparticles are formed by nucleation and the rest of the silver clumps around a central point. Perhaps something similar happened here, although at some point below the surface, and at room temperature these smaller particles never joined with the surface clumps. It is also interesting to note that there appears to be a thin layer of polymer across the top of the silver layer. This is surprising given the high conductivity of these films. This observation suggests that light plasma or chemical etching could enhance surface conductivity.

One unsuccessful route to unmasking the "missing" silver was soaking the metallized polymer in a potassium iodide solution. The hope was that some unreduced silver would enter the solution and then precipitate as silver iodide on the surface of the film. However, no precipitate was observed. This is not surprising given that the iodide ions can't penetrate the film any further than the reducing agent could have. The same logic holds true for migrating silver ions: if they didn't reach the surface to be reduced, they likely wouldn't reach the surface to form a precipitate. Although it is certainly a problem to have “lost” silver, the good conductivity values mitigate our concern somewhat. Additionally, the fact that the silver is not reduced in the bulk leaves the door open to reduce it at a later point in time.

How could the rest of the silver be located? The answer likely rests with more TEM work. Given unlimited access to the instrument, films would be reduced and then heated to 300 for several hours. All previous research indicates this temperature will reduce all silver ions in the film. Thus it should unmask the unreduced silver and create
a plethora of silver particles in the surface of the film. Additionally, the heat could stimulate migration and allow them to join the silver layer formed initially by chemical reduction.

*Exploring Other Applications: Palladium and Foaming*

The films show a great aptitude for patterning in both commercial and artistic applications (Figure 13). Using a commercial etching solution containing iodine and acid, unwanted silver plating was dissolved leaving only the desirable portion. The solution was rated to etch at 200 angstroms per second, allowing some measure of control of the depth of etching. At this rate, a 100nm film would take approximately 15 minutes to remove. This would be useful for circuitry or adding metallic flair to artistic projects. Detailed patterning can even be achieved without the use of etching agent. Use of a commercial Sharpie marker as a masking agent to coat some regions prior to application of the reducing agent effectively blocks the reduction process and can be removed afterwards with methanol without damaging the silvered area.

Satisfied with our optimized metallization technique, other applications were explored. Particularly, we were interested in foaming polymers. Silver is often interchangeable with palladium due to similar weights and properties. Previous group work explored the use of palladium(I) methyl sulfide complexes for metallization. Palladium serves as a catalyst for hydrogenation. It is reasonable, then, that these metallization techniques could serve to create catalysts for fuel cell applications. Current palladium coated polymers, however, do not exhibit enough catalytic activity to make
Figure 13: A is a photograph of a silvered polyimide film taped to a glass petrographic slide, 27 x 46 mm with double-sided tape; B is a photograph of the patterned film A using a Sanford permanent red marker (blue color is an artifact of amateur photography); C is a photograph of the Transene Company, Inc. Silver Etchant Type TFS treated film to remove excess, unpatterned silver followed by washing off the ink mask with ethanol yield the final silver-patterned film. The patterning shown was produced by Luke Davis and is presented here with permission.

All photographs were done free hand and thus are not at a professional standard.
them cost effective. The simplest way to increase catalytic activity would be to increase surface area. One way of doing this would be to metallize a foam.

Foaming polymers require a chemical blowing agent. Commercially, azodicarbonamide (ACA) is one of the more common blowing agents, thanks to the large volume of gas emitted upon decomposition. At temperatures of 160-190°C and higher, ACA breaks down into nitrogen, carbon monoxide, carbon dioxide, and ammonia gases. ACA was added to our polymer films with limited results. Although the molds of air bubbles were present, it appeared that our polyimide films were unable to support foaming. The bubbles of gas could not be trapped by thin films. Therefore, thicker polymers were cast up to 1cm deep. Some foaming was observed for BTDA-ODA, another polyimide. The polymer was dissolved in a combination of solvents, DMAc and NMP, and heated at 180°C for 40 minutes to evaporate the solvent and decompose the ACA. The process depended on a number of factors, including the ratio of the two solvents, the amount of solvent present, and the amount of blowing agent added. Citric acid was also used as a blowing agent with limited success. Though a fluffy foam substance could be created from the BTDA-ODA polymer, the success did not translate to the 6FDA-0.5ODA/0.5DABA polymer. Heating simply decomposed the polymer to a black tarry substance instead of foaming it. Work in this area remains an ongoing endeavor.
CONCLUSION

This study attempted to recreate the room temperature metallization model with an alternative silver complex. On a macroscopic level, the two systems appeared to behave very similar to one another. The new HFA films were just as conductive and reflective, if not more so, than their triflic counterparts. Furthermore, several parameters in the reduction process were studied. Thus, the problem of excess triflic acid in the polymer was solved and an alternative route to metallization was both achieved and optimized. Though the two systems appeared to behave in much the same manner, microscopy revealed they form very differently. The HFA films show a great deal more nucleation sites. However, they also failed to reduce all the silver in the film, a problem the triflic acid films did not have. The reasons for the difference are not clear.

Other studies were not as fruitful. Attempts to create a polymer foam with several blowing agents was a failure. Transferring from a silver to a palladium system posed a number of challenges which were not solved due to time constraints. Other constraints, such as availability of microscopy instrumentation also held back research. Future research, however, can take utilize the fact that there is a ligand effect in this process, and hence many new silver complexes and salts can now be studied.
REFERENCES


APPENDIX A

Latent Patterned Surface Metallization of Silver Ion-Doped Polyimide Films

Departments of Chemistry and Biology, College of William and Mary, Williamsburg, VA 23187

ABSTRACT

A straightforward ambient temperature route to the fabrication of surface silver-metallized polyimide films is described. Silver(I) trifluoromethane sulfonate and a polyimide, derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and an equimolar amount of 4,4'-oxydianiline (ODA) and 3,5-diaminobenzoic acid (DABA), were dissolved together in dimethylacetamide. Silver(I)-doped films were prepared at thicknesses of 25-50 microns and depleted of solvent by evaporation. The silver(I)-containing films were then treated with aqueous reducing agents, which brought forth silvered films exhibiting conductivity on the order of bulk polycrystalline silver and good specular reflectivity.

INTRODUCTION

The construction of a thin metal films on flexible polymeric bases and a detailed understanding of the metal-polyimide interfacial region is an active area of interest. Physical vapor deposition is the common approach for forming metal surfaces on dielectric bases. However, for passive metals such as gold, silver, copper, etc. metal to polymer adhesion is generally unacceptable. Herein we report a synthetic route, remarkable in simplicity and efficacy, to silvered polyimide films which possess unfailing adhesion of metal to polymer, excellent electrical conductivity, and significant specular reflectivity. The work presented herein has potential for the straightforward fabrication of: 1) metallic electrical circuits on dielectric platforms, 2) metallic antennas on and embedded in dielectric materials, 3) metallic coatings for electromagnetic shielding, and 4) EM radiation reflective mirrors on flexible dielectric bases.

EXPERIMENTAL

Materials. 3,5-Diaminobenzoic acid (DABA, 98%) and dimethylacetamide (DMAc 99.8%, anhydrous) were obtained from Aldrich-Sigma. DABA was recrystallized from water and vacuum dried at 100 °C. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride was obtained from Hoechst Celanese and vacuum dried for 5 h at 160 °C prior to use. Oxydianiline (ODA) was obtained from Chriskev and used without further treatment.
Preparation of the polyimide form of the copolymer formed from 6FDA with an equimolar mixture of 4,4'-oxydianiline and 3,5-diaminobenzoic acid. 1. Synthesis of the poly(amic acid) - DABA (3.016 g, 198.2 mmol) and ODA (3.972 g, 198.4 mmol) were added as solids directly to DMAC (60 mL). After diamine dissolution, 6FDA (17.603 g, 396.3 mmol) was added under a slowly flowing nitrogen stream. An additional 40 mL of DMAC was added. The final mixture was then stirred at room temperature for 15 h. 2. Synthesis of the polyimide form by chemical imidization - the poly(amic acid) copolymer above was imidized in an acetic anhydride/pyridine (150 mL of each). The polyimide solution was then added slowly into 500 mL of water in a rapidly stirring blender. The precipitated polyimide was filtered and washed with water. The final co-polyimide was dried at 150 °C for 10 h.

Synthesis of 6FDA/0.5 ODA-0.5 DABA silvered films. Synthesis of 6FDA/0.5 ODA-0.5 DABA silvered films. A 6FDA/0.5 ODA-0.5 DABA film containing 8.0 wt % silver (considering only silver metal and polyimide) is described here as illustrative of all metallized film syntheses. Silver(I) oxide (0.172 g, 0.742 mmol) was added to a 12-mL glass jar, followed by 2.0 g of DMAC, trifluoromethane sulfonic acid (0.222 g, 1.48 mmol), and finally another 2.0 g of DMAC, respectively. The reaction mixture was stirred for 15 min to form in situ (trifluoromethane sulfonato)silver(I). To this silver(I) solution, 2.00 g of the fully imidized form of 6FDA/0.5 ODA-0.5 DABA copolymer was added followed by 4.0 g DMAC. The resulting solution was stirred for 1 h. The silver-doped solution was cast onto a glass plate at a thickness of 0.45 mm. The film was placed in a film box for 15 h with dry air flowing through the box to evaporate DMAC. The tack free film was then surface-treated with the reducing agent.
RESULTS and DISCUSSION

In previous work\textsuperscript{1,2} we established a thermally-promoted silver(I) reduction route to prepare surface-silvered fluorinated polyimide films containing 6FDA as the dianhydride component. A silver(I) complex was dissolved with either a poly(amic acid), or the soluble parent polyimide form of the poly(amic acid), in an aprotic polar solvent. A cast film of either the silver(I)-doped poly(amic acid), or the silver(I)-doped polyimide, depleted of solvent by evaporation, was heated to 275-300 °C which brought a reflective, but never conductive, silver surface on a fully imidized polymeric form. The fully imidized structure is the only form with applied usefulness due primarily to hydrolytic instability of poly(amic acid). A question that arises for a soluble, fully imidized polyimide is whether a low temperature route could be found to a conductive and reflective silvered polyimide. We first attempted to effect a silvered surface by treating the silver(I)-doped 6FDA films with an aqueous reducing reagent. This approach was not successful. However, reduction of silver(I)-doped 6FDA/4-BDAF and 6FDA/1,3(3)-APB (Figure 1) fully imidized films with inorganic reducing agents such as sodium borohydride, hydrazine hydrate, and hydroxylamine did give darkened films indicating that the reducing agent penetrated the silver(I)-doped structure but not in such a manner as to generate a metallic surface. It appears that there is not sufficient silver(I) ion mobility in the amorphous, glassy, hydrophobic 6FDA/4-BDAF and 6FDA/1,3(3)-APB polyimides (Figure 1), which we used, to transport ions rapidly to the film surface to undergo subsequent reduction.

At this point we thought that the inclusion of pendant, hydrophilic carboxylic acid groups along the polyimide chain would enhance the absorption of water in the polymer film leading to modest polyimide swelling, thereby allowing for more facile silver ion migration. Thus we synthesized the fully imidized, random polyimide 6FDA/0.5 DABA-0.5 ODA (Figure 1). The 6FDA/0.5 DABA-0.5 ODA fully imidized copolymer and silver(I) triflate, prepared in situ from silver(I) oxide and triflic acid in a 1:2 mole ratio were first dissolved in DMAc. After stirring for 5 min, a latent silver ion film was cast on a glass plate and placed in a film box for ca. 15 h to evaporate DMAc. After this, aqueous hydroxylamine was placed on the top of the film. The silver(I)-doped films quickly became opaque with formation of a silver mirror which exhibits high conductivity. The silvered films exhibited unfailing metal-polymer adhesion. The results of several latent metallization experiments are summarized in Tables 1-3. Table 1 summarizes electrical resistance data (two-point probe) for the metallization of silver(I) trifluoromethane sulfonate–6FDA-based polyimide films prepared with an equimolar amount of the ODA and 3,5-DABA diamines as a function of three reducing agents, specifically, aqueous solutions of hydrazine hydrate, hydroxylamine, and methylhydrazine. The silver concentration in the cast films ranged from 2.1 to 7.4 wt % corresponding to 0.3 to 1.1 vol % based on a density of 10.5 g/cm\textsuperscript{3} for silver and 1.45 g/cm\textsuperscript{3} for the polyimide. We chose these three reducing agents because of the minimal byproducts of the reduction,
which are primarily dinitrogen, water or methanol, and hydronium ions. Two significant conclusions are suggested by the data in Table 1: 1) varying concentrations of silver(I) ions lead to metallized polyimide surfaces which are highly conductive, and 2) hydroxylamine and hydrazine at very modest concentrations are highly effective in developing a silver surface. It is interesting to note that once the concentration of 3.9 wt % silver(I) is reached, higher silver(I) concentrations do not lead to films that have decreased resistance. With the preliminary observations contained in Table 1, we chose then to examine more thoroughly the formation of silvered films with a silver ion concentrations at 4.0 and 8.0 wt % using hydroxylamine as the reducing agent, data for which are in Table 2.

Table 2 summarizes resistivity and reflectivity data for the metallization of 6FDA/0.5 DABA-0.5 ODA films at 4 wt % silver(I) using hydroxylamine. One thing stand out: treating the films with dilute ammonia for 5 min before application of the reducing agent greatly increases the rate of formation of a metallized surface although there is no enhancement of conductivity.

Table 3 displays resistivity and reflectivity data which show the effect of subsequent thermal annealing on a series of identical 8.0 wt % silver-6FDA/0.5 DABA- 0.5 ODA films. A single latent silver(I)-polyimide solution was cast simultaneously onto ten glass petrographic slides, and, after drying ca. 15 h in the film box, each slide was reduced independently from the same stock solution of 1.0 vol % hydroxylamine. Because the films were independently metallized to the first complete visual opacity, the initially realized resistivity values (Table 4, left) prior to thermal treatment vary slightly. Over the ten films of Table 3 the average resistivity is 3.6 ohms/sq (neglecting the outlying values of 15 and 18 ohms/sq) and average reflectivity is 63 %. Heating the films according to the protocol detailed in Table 2-footnote c, resulted in an
Table 1. Metallization of 6FDA/0.5 DABA-0.5 ODA films as a function of reducing agent and silver(I), as the CF$_3$SO$_3$ - salt, concentration. Resistance measurements via two point probe technique.

<table>
<thead>
<tr>
<th>Ag(I)-co-polyimide film sample</th>
<th>Silver(I) (wt %)$^a$</th>
<th>Silver(I) (vol %)</th>
<th>Aqueous reducing solution (agent) (vol %)</th>
<th>Resistance (two point) (ohm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.1</td>
<td>0.30</td>
<td>NH$_2$OH 0.5</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>0.30</td>
<td>N$_2$H$_4$ 0.5</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>0.30</td>
<td>CH$_3$NHNH$_2$ 1.0</td>
<td>c</td>
</tr>
<tr>
<td>B</td>
<td>3.9</td>
<td>0.55</td>
<td>NH$_2$OH 0.5</td>
<td>2.1</td>
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<tr>
<td></td>
<td>3.9</td>
<td>0.55</td>
<td>N$_2$H$_4$ 0.5</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>3.9</td>
<td>0.55</td>
<td>CH$_3$NHNH$_2$ 1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>C</td>
<td>5.6</td>
<td>0.81</td>
<td>NH$_2$OH 0.5</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
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<td>1.4</td>
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<td>0.81</td>
<td>CH$_3$NHNH$_2$ 1.0</td>
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<tr>
<td>D</td>
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<td>1.1</td>
<td>NH$_2$OH 0.5</td>
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<tr>
<td></td>
<td>7.4</td>
<td>1.1</td>
<td>CH$_3$NHNH$_2$ 1</td>
<td>11</td>
</tr>
</tbody>
</table>

a. The percent silver is calculated on polymer and silver only; the anion is not included.
b. Volume percent is calculated from the density of silver at 10.5 g/cm$^3$ and the density of the polyimide at 1.45 g/cm$^3$.
c. Resistances are in the megaohm region.

Table 2. Metallization of 6FDA/0.5 DABA-0.5 ODA films at 4.0 wt% silver(I) as the CF$_3$SO$_3$ - salt

<table>
<thead>
<tr>
<th>Aqueous reducing solution (agent) (vol %)</th>
<th>Ammonia (aqueous)</th>
<th>Metallization time (min)</th>
<th>Reflectivity$^b$ (%)</th>
<th>Resistivity$^c$ (ohm/sq)</th>
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</thead>
<tbody>
<tr>
<td>NH$_2$OH 1.0</td>
<td>none</td>
<td>6.7</td>
<td>88</td>
<td>3.9</td>
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<tr>
<td>NH$_2$OH 0.5</td>
<td>none</td>
<td>8.3</td>
<td>84</td>
<td>5.9</td>
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<tr>
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<td>9.5</td>
<td>88</td>
<td>2.7</td>
</tr>
<tr>
<td>NH$_2$OH 1.0</td>
<td>0.1 M</td>
<td>2.3</td>
<td>73</td>
<td>4.9</td>
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<tr>
<td>NH$_2$OH 0.5</td>
<td>0.1 M</td>
<td>2.8</td>
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<tr>
<td>NH$_2$OH 0.1</td>
<td>0.1 M</td>
<td>2.5</td>
<td>61</td>
<td>5.4</td>
</tr>
</tbody>
</table>

a. Ag(CF$_3$SO$_3$) prepared without isolation from equivalent amounts of Ag$_2$O and CF$_3$SO$_3$H in DMAc.
b. Specular reflectivity relative to a Perkin-Elmer Al mirror with an absolute reflectivity of 0.92.
c. Surface resistivity measured via the four-point probe technique.
increase in specular reflectivity up to ca. 150 °C; thereafter the reflectivity decreases relative to the room temperature values until, after being at 300 °C for 1 h, the films have lost virtually all reflectivity. The change in resistivity is more uniform, with all films but one showing a decrease in surface resistivity. The resistivity measurement upon first reaching 300 °C (Table 3, sample 8) appear anomalous and have been left out of Figure 2; we have no explanation for this, although multi-component, solid state heterogeneous systems undergoing chemical transformation not uncommonly exhibit inconsistent behavior. Figure 2 shows the percent change in sheet resistivity as a function of thermal treatment time. The percent change in sheet resistivity increases up to ca. 250 °C; thereafter, the percent change decreases, but the sheet resistivity is still lowered. We suggest that the modest increase in conductivity is due to some sintering of silver particles to densify the metallic phase, which is consistent with observations of Mazur and coworkers in silver-polyimide systems. Further studies are underway to understand the decrease in reflectivity after reaching a maximum value at 150 °C and to understand the less pronounced variations in resistivity with cure temperature.
Figure 3 shows a scanning electron micrograph for 4 wt % silver(I)-
6FDA/0.5 DABA-0.5 ODA films reduced with 1.0% hydroxylamine. The surface silver is a predominately
continuous layer with something like typical grain boundary morphology, although there are some random gaps mostly on the order of tens of nanometers.

CONCLUSION

A straightforward and cogent method has been developed to fabricate silver surface-metallized 6FDA/0.5 DABA-0.5 ODA polyimide films with surface resistivities on the order

![Percent Change in Sheet Resistivity versus Heating Time](image)

Figure 2. Percent change in sheet resistivity versus heating time for an 8 wt % silver film prepared 
from 6FDA/0.5 4,4'-ODA-0.5 DABA-AgOTf and reduced with 1.0 vol % hydroxylamine.

![Figure 3. SEM at three different magnifications of 4 wt % AgOTf in 6FDA/0.5 DABA-0.5 ODA 
reduced with 1.0% NH2OH. Scale bars are all 1000 nm.](image)

Figure 3. SEM at three different magnifications of 4 wt % AgOTf in 6FDA/0.5 DABA-0.5 ODA 
reduced with 1.0% NH2OH. Scale bars are all 1000 nm.

of bulk polycrystalline silver have been achieved. Of crucial importance, the silver film is unfailingly adhered to the base polyimide, something which cannot be achieved with physical vapor deposition of native silver onto high-performance polymers.
REFERENCES