Silver-Polyimide Nanocomposite Films: Single-Stage Synthesis and Analysis of Metalized Partially-Fluorinated Polyimide BTDA/4-BDAF Prepared from Silver(I) Complexes

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College of William & Mary - Arts & Sciences

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https://dx.doi.org/doi:10.21220/s2-076f-2a69

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This Thesis is submitted in partial fulfillment of the requirements for the degree of Master of Science

Joshua Erold Robert Abelard

Approved by the Committee, June 2010

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Professor David Thompson
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Reflective and Conductive films have been prepared by introducing either silver hexafluoroacetylacetonato (AgHFA) or silver trifluoroacetylacetonato (AgTFA) into BDTA/4-BDAF poly(amic acid). The poly(amic acid) was converted to a polyimide via a thermal curing process which simultaneously caused the reduction of silver complexes to particles of silver metal. The properties of these films have been compared to other similar systems prepared from a variety of polyimides and silver complexes. A key theme reported herein is the direct comparison for classical polyimides, fluorinated polyimides, and hybrid polyimides containing both classical and fluorinated elements. Films were analyzed using X-ray diffraction, differential scanning calorimetry, spectral reflectivity, scanning electron microscopy and transmission electron microscopy.
# Table of Contents

Dedication ................................................................................................................... ii  
Acknowledgements ................................................................................................................ iii  
List of Tables ........................................................................................................................... iv  
List of Figures ............................................................................................................................ v  
Prologue .................................................................................................................................... 1  
Background Information .......................................................................................................... 4  
Experimental .......................................................................................................................... 27  
Results and Discussion ........................................................................................................... 30  
Works Cited ............................................................................................................................ 48  

Appendix : On a Facile Approach to Silver-Patterned Dielectric Substrates

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Introduction</td>
<td>50</td>
</tr>
<tr>
<td>Experimental</td>
<td>51</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>54</td>
</tr>
<tr>
<td>Conclusion</td>
<td>60</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>60</td>
</tr>
<tr>
<td>References</td>
<td>61</td>
</tr>
<tr>
<td>Figures</td>
<td>62</td>
</tr>
<tr>
<td>Tables</td>
<td>66</td>
</tr>
</tbody>
</table>
Dedication

This thesis is dedicated to my loving parents for their unwavering emotional and financial support from birth until now. Thank you so much for devoting such a large part of your lives to helping me. This thesis is also dedicated to my research advisor, David Thompson. Thank you for being a great advisor and for helping me discover my love for chemistry research.
Acknowledgements

Thank you Evguenia Orlova for taking the time to prepare SEM and TEM slides and for helping me capture great images of those samples.

Thank you Dr. Wei Cao for taking the time to operate the TEM and for giving great advice on how to prepare my samples.

Thank you Amy Wilkerson, Olga Trofimova, and Brandt Robertson for teaching me to operate the SEM and for helping me get great images.

Thank you Professor Robert Pike for showing me how to get X-ray diffraction spectra.

Thank you Professors Gary Rice and Christopher Abelt for taking the time to read this thesis and for agreeing to be on my approval committee.

Many thanks to the entire faculty in the Chemistry Department at William and Mary for your love of teaching. I really have learned a lot from all of you.

And, most of all, thank you Professor David Thompson for being a great advisor during my studies at William and Mary.

Any mistakes remaining in this thesis are the result of my own errors and are in no way the responsibility of any of the great people who have helped me write it.
List of Tables

Table 1. Thermomechanical Properties of Flexible Silver-Modified Polyimide Films ........9
Table 2. Percent Reflectivity for Polyimide Films Doped with Ag(COD)(HFA) at Varying Angles ................................................................................................................................. 9
Table 3. Reflectivity as a Function of Concentration for wt% silver ........................................12
Table 4. Modulus and tensile strength as a function of wt% silver ........................................13
Table 5. Tg and PDT as a function of wt% silver .....................................................................13
Table 6. Comparison of various ligands used to metalize BTDA-ODA ..................................14
Table 7. Reflectivity, Thermal, and Resistivity Data for (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)-BTDA/ODA films cured to 300 °C for 7 h .........................................................16
List of Figures

Figure 1. Illustrative scheme for the preparation of surface-silvered polyimide films via a single-stage self-metalizing route ................................................................................................................................... 3

Figure 2. Structures for monomers and additives used in Rubira 1994 4 ............................................... 8

Figure 3. Reaction to create AgHFA complex in preparation for in situ reduction of silver ......... 12

Figure 4. Development of reflectivity as a function of temperature/time for 13% silver metallized BTDA/4,4-ODA films ............................................................................................................................................ 17

Figure 5. X-ray diffraction patterns in the silver 111 and 200 region for 10.7% AgTFA-BTDA/ODA ....................................................................................................................................................................... 18

Figure 6. Transmission electron micrographs of 10.7% AgTFA-BTDA/ODA films at different cure stages ........................................................................................................................................ 19

Figure 7. Significant polymers and chemicals studied in Davis 2007 11 ................................................. 21

Figure 8. Comparisons between poly(amic acid) and polyimide as the starting polymer .......... 22

Figure 9. Specular reflectivity versus time/temperature data for higher concentration silver-6FDA/4-BDAF films ............................................................................................................................................... 24

Figure 10. Specular reflectivity versus time/temperature data for lower concentration silver-6FDA/4-BDAF films ........................................................................................................................................ 25

Figure 11. Comparison of metallized films derived from fluorinated polyimides ............. 26

Figure 12. Images of metalized BTDA/4-BDAF films at different cure stages .................... 32

Figure 13. Images of metalized BTDA/4-BDAF films at different cure stages ......................... 33

Figure 14. Images of metalized BTDA/4-BDAF films at different cure stages ......................... 34

Figure 15. Images of metalized BTDA/4-BDAF films at different cure stages ......................... 35

Figure 16. Specular reflectivity versus time data for metalized BTDA/4-BDAF films containing 2%, 4%, 6%, 8%, and 13% Ag from AgHFA ............................................................................................................ 38

Figure 17. Specular reflectivity versus time data for metalized BTDA/4-BDAF films containing 8% and 13% Ag from AgTFA ........................................................................................................... 39

Figure 18. Close up image of a BTDA/4-BDAF film containing 13% Ag from AgHFA .......... 40

Figure 19. Close up image of a BTDA/4-BDAF film containing 13% Ag from AgTFA .......... 41

Figure 20. TEM images of BTDA/4-BDAF metalized with 13% Ag from AgTFA at different cure stages ........................................................................................................................................... 44

Figure 21. X Diffraction patterns for 13% AgTFA-BTDA/4-BDAF and 13% AgHFA-BTDA/4-BDAF. 45

Figure 22. SEM micrographs of BTDA/4-BDAF metalized with 13% Ag from AgTFA at different cure stages ........................................................................................................................................... 46
Prologue

The research presented in this thesis investigates applying metal layers to polymer film substrates. The primary objective is to create a surface metalized film that is both conductive and reflective. This is a topic of great interest because of its many potential uses. Said uses include the following: a) lightweight and flexible mirrors that can easily be transported to space and used in communications antennae; b) solar concentrators for terrestrial solar energy power plants or propulsion devices in space; c) flexible electronic circuits; d) conductive and flexible polymeric tapes. Generally speaking, noble, inert metals such as silver, gold, copper, and platinum are the preferred choice for these applications because of their low resistivities and high coefficients of reflectivity. High performance polymers such as polyimides and poly(arylene ether ketones) are ideal because of their high resistance to thermal oxidative degradation, excellent chemical stability, and excellent mechanical properties. High performance polymers have the advantage of being lightweight, flexible, elastic, and generally robust, making them a better choice for many applications than glass and ceramic substrates.

The investigation reported here focuses on applying silver metal layers to BTDA/4-BDAF polyimide film substrates via an in-situ, single stage process. Silver was chosen for its high conductivity (higher than any other metal) and excellent reflectivity above 350 nm. BTDA/4-BDAF was chosen as the substrate to analyze the properties of a metalized film where the dianhydride is a “classical” structure and the diamine is a “fluorinated” structure. Past research has studied metalized films made from
completely classical polyimides or completely fluorinated polyimides. This is the first investigation on metalizing this type of hybrid polymer via the following procedure. Fluorinated and classical metalized polyimide films each have distinct properties, and it is of interest to find out what happens when both are combined in one system, that is in a hybrid system.

Figure 1 below provides a visual description of the process used to create metalized films during this project. Silver acetate is reacted with either hexafluoroacetylacetonate (HFAH) or trifluoroacetylacetonate (TFAH) using dimethylacetamide (DMAC) as the solvent from the (hexafluoroacetylacetonato)silver(I) complex (AgHFA) and the (trifluoroacetylacetonato)silver(I) complex (AgTFA) respectively. Silver acetate is not soluble in DMAC, but both silver complexes are. Completion of the reaction can thus be visually confirmed when no solids remain. The silver complexes are not isolated at any point in the procedure. Instead, the solution of AgHFA or AgTFA with DMAC is mixed directly into a DMAC solution of poly(amic acid). The silver-doped poly(amic acid) is then cast into a film and dried. Thermally curing these films simultaneously closes the amic acid rings to give the imide form and reduces the silver(I) salt to silver(0) metal.

This process metalizes the polyimide film without adversely affecting its mechanical properties. A wide variety of analytical methods can be used to characterize the final metalized and cured films including scanning electron microscopy, transmission
electron microscopy, thermal gravimetric analysis, differential scanning calorimetry, X-ray diffraction, reflectivity, and resistivity.

STEP 1. A silver(I) complex is prepared in situ in dimethyl acetamide (DMAc) containing poly(amic acid). The resulting homogeneous solution is cast as a film.

STEP 2. The homogeneous solution from STEP 1 is thermally cured to imidize the amic acid and reduce silver(I) to give a metalized film surface.

Figure 1. Illustrative scheme for the preparation of surface-silvered polyimide films via a single-stage self-metalizing route incorporating in-situ formation of the silver(I) metallization precursor.
Background Information

Polyimides are already widely used throughout aerospace and other cutting edge technology applications for their excellent dielectric properties and ability to withstand high temperatures, strong radiation, and a wide range of solvents. Polyimides also have robust mechanical properties that make them suitable for many high-stress situations. Some applications are a good match for the mechanical, chemical, and thermal properties of polyimides, but also require a conductive or reflective surface. Solar mirrors are one such application. This requires that the polyimide be coated with a conductive and reflective metal.

The electrical and optical properties of silver make it well suited for a wide variety of application in technology as mentioned above. Silver has a higher degree of reflectivity in the solar spectrum than any other metal. It also has one of the lowest resistivities among the metals and is inexpensive compared to most other noble metals. There are other metals that have acceptable resistivity and reflectivity, but they will not be investigated in this project. Aluminum in particular is highly reflective and conductive and has the added benefit of being chemically resistant because of its very thin oxide coating. Unfortunately it is not a suitable material for the electroless reductive metallization process used here because of its highly negative standard electrode potential. Copper has high conductivity and is reasonable inexpensive, but copper salts tend to form oxides when reduced instead of particles of native metal. Rhodium has a high degree of hardness and impressive chemical stability, particularly against acids, but
is prohibitively expensive. Gold has strong reflectivity in the infrared range and excellent conductivity, but is also expensive. For those reasons, silver has been selected as the best metal to focus on in this project to prepare surface metalized polymer films that have surface conductivity and high reflectivity particularly in the visible spectrum.

Typical methods used to prepare surface metalized polymer films generally involve depositing silver from an external source onto the polymer film surface. A few examples of this are: physical vapor deposition via sputtering or thermal evaporation, thermally induced chemical vapor deposition (CVD), photochemically induced CVD, plasma induced CDV, electrodeposition, and electroless chemical reduction from a solution in which the substrate is immersed. All of these processes require at least two steps to metalize polymer films. The substrate film must first be prepared. This often includes modification with ion beams, plasma, electron beams, or other high energy devices to improve metal-to-substrate adhesion. Photolytic and chemical treatment methods can also be used for the modification process. Then the metal is added to the substrate film by CVD or one of the other aforementioned processes in a separate step. Unfortunately, noble metals, such as silver, copper, platinum, and gold, show poor adhesion to films. Also, the above processes are difficult to do on a large scale due to the nature of the steps involved. The procedure investigated in this project uses a single step, in-situ process. Past work on this procedure indicates a high degree of metal/polymer adhesion and the potential to work for large scale projects with less difficulty than the alternative procedures.
Endrey (DuPont), one of the pioneers of preparing metalized polyimides via the
in situ method being studied herein, reported his findings in a DuPont patent from the
1960s². Endrey proposed a path to preparing reflective and conductive films by starting
with a solution of poly(amic acid), doping that solution with a silver salt compound,
casting films or other shapes, then curing the amic acid / metal salt to its imide form. His
curing process simultaneously reduced the silver (I) salt to silver metal and reportedly
resulted in metalized polyimide films which were conductive and reflective. Although he
only reported actually working on a limited range of examples, Endrey suggested that a
wide range of polyimides and silver salts can be used. Endrey’s procedure is as follows.
Polyamic acids, were prepared in a solvent using pyromellitic dianhydride with either
meta-phenylenediamine or with 4,4’ – diaminodiphenylmethane. A silver salt, either
silver acetate or silver caprylate, was added to the polyamic acid. The patent suggests
that this led to formation of a amic acid / silver(I) salt complex which tended to promote
gelation of the polymer. The gel was broken up by adding a ligand such as pyridine
which is capable of forming a strong complex with silver(I) ions. The final result of
mixing the silver salt with the poly(amic acid) solution was a clear and viscous doped
mixture of silver salt compound in poly(amic acid) and a large excess of pyridine or
similar solvent. The polyamic acid salt complex was cast into a film and heated to 300 °C
in a vacuum oven for 30 min. Analyzing the resulting polyimide film with X-ray
diffraction revealed the presence of silver metal nanoparticles. The films were reported
to be conductive at this point. Further information about reflectivity and mechanical
properties was not provided. Unfortunately, attempts to duplicate Endrey’s reported
results have encountered difficulties. The cured metalized polyimide films don’t display measurable conductivity, and the films are of poor quality. They do have a visible amount of silver metal, but are cracked and not practically useful. This seems to be confirmed by the fact that no other research group reports further work on the topic for approximately two decades. Endrey’s original work also was never reported in a peer-reviewed journal and has not been used in industry to our knowledge. A conclusion that can be reached from Endrey’s results is that complexes of silver(I) with acetate and pyridine create polyimide films with degraded mechanical and optical properties. Rubira et al. report a somewhat different technique to preparing metalized polyimide films. The primary difference is their use of the silver complex (1,5-cyclooctadiene)(hexafluoroacetylacetonato)silver(I), or Ag(COD)(HFA). They also make the interesting hypothesis that a polyimide with sulfur in its molecular structure will enhance adhesion to silver. To this end, they metalized and compared four different polyimides containing dianhydrides BDSDA or BTDA and diamines ODA or ASD. ASD and BDSDA both contain sulfur as shown in Figure 2.

Data was reported on mechanical properties before and after metallization, including reflectivity, conductivity, and general appearance of films. Metalized films (Table 1) had a lower polymer decomposition temperature than the respective parent films. This is not surprising because silver is known to serve as a catalyst for oxidative degradation of films. The glass transition temperature, Tg as measured by differential scanning calorimetry, was not significantly affected by the metallization process.
Reflectivity data, shown in Table 2, and general appearance show a distinct difference between the BTDA and BDSDA films. The BDSDA films were cloudy in appearance and, not surprisingly, had negligible reflectivity of less than 10% relative to a vapor deposited aluminum optical calibrating mirror. The BTDA-ODA and BTDA-ASD films were both significantly better at 50-60% reflectivity depending on angle, but still not ideal. The angle dependence of reflectivity is of interest. Mirrors with a surface of naked silver metal have the same reflectivity at all angles.

\[
\begin{align*}
\text{H}_2\text{N-ODA} & & \text{H}_2\text{N-ASD} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & & \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{BTDA} & & \text{Ag\{COD\{HFA\}\}} \\
\end{align*}
\]

**Figure 2.** Structures for monomers and additives used in Rubira 1994.
Table 1. Thermomechanical Properties of Flexible Silver-Modified Polyimide Films as reported in Rubira 1994.

<table>
<thead>
<tr>
<th>films</th>
<th>$T_g \ (°C)$</th>
<th>PDT (°C)$^a$ in N$_2$</th>
<th>PDT (°C)$^a$ in air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>not doped</td>
<td>doped</td>
<td>not doped</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>270</td>
<td>265</td>
<td>628</td>
</tr>
<tr>
<td>BTDA-ASD</td>
<td>270</td>
<td>270</td>
<td>644</td>
</tr>
<tr>
<td>BDSDA-ODA</td>
<td>214</td>
<td>221</td>
<td>577</td>
</tr>
<tr>
<td>BDSDA-ASD</td>
<td>218</td>
<td>221</td>
<td>620</td>
</tr>
</tbody>
</table>

$^a$ Polymer decomposition temperature (PDT) which corresponds to 10% weight loss.

Table 2. Percent Reflectivity for Polyimide Films Doped with Ag(COD)(HFA) at Varying Angles as reported in Rubira 1994.

<table>
<thead>
<tr>
<th>film</th>
<th>percent reflectivity$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°</td>
</tr>
<tr>
<td>BTDA-ODA</td>
<td>65.2 ± 0.8</td>
</tr>
<tr>
<td>BTDA-ASD</td>
<td>55.0 ± 1.2</td>
</tr>
<tr>
<td>BDSDA-ODA</td>
<td>3.9 ± 2.1</td>
</tr>
</tbody>
</table>

$^b$ Relative to an optical mirror which was used as 100% reflectivity standard. Wavelength at 531 nm.
The best explanation for the results reported by Rubira et al. is a layer of polyimide over the silver. This thin polyimide layer is referred to by the authors as an “overlayer.” Polyimides are not transparent at visible wavelengths. Light encountering the film at angles deviating further from exactly perpendicular would have to travel through correspondingly greater distances of polyimide before and after being reflected by the silver. This will lead to progressively lower reflectivity at greater angles as shown in the data. This observation agrees with the prediction that silver particles cannot emerge from the polymer to lie on the surface because the surface energy of the polymer is significantly lower than that of silver metal\textsuperscript{5}. Two conclusions especially relevant to this thesis can be made from the Rubira 1994 report: 1) sulfur-containing polyimides are not advantageous for applications that require reflectivity; 2) the Ag(COD)(HFA) complex works well for metalizing polyimides without causing film degradation other than what would be expected due to the catalyzing effects of silver nanoparticles on polymer oxidation at elevated temperatures.

Southward et al.\textsuperscript{6} present a modification to the above procedure that results in significant improvements in reflectivity. Previous experiments used silver complexes that were synthesized separately and isolated prior to addition to the poly(amic acid) resin. This is not ideal as silver complexes can degrade when stored\textsuperscript{7} in the presence of air or heat. The Southward et al. report introduces the in-situ method used in this thesis where the silver complex is prepared in solution and used in that state without being isolated. The reaction used is depicted in Figure 3. Silver acetate was reacted with HFAH...
in DMAC solvent to form a solution of AgHFA complex in DMAC which was then added quantitatively to a BTDA-ODA poly(amic acid) resin. The reaction to form AgHFA also created acetic acid as a by-product, but this had no significant effect since acetic acid has a boiling point of ca. 120 °C and boiled off during the cure cycle which reached 300 °C. Reflectivity results are shown in Table 3.

This in-situ modification raised reflectivity to as high as nearly 80% as compared to Rubira’s results of ca. 65%. The angular dependence of reflectivity observed in Rubira’s research was still present and can be explained once again by the presence of a visible semi-transparent polyimide layer covering the silver metalized surface. This polymer layer is a reasonable explanation for why none of the films discussed to this point display significant conductivity regardless of reflectivity. The polymer layer also potentially explains why the reflectivity isn’t even higher in the good-quality films that appear highly mirrored to visual inspection. Extra durability of the metalized film is one interesting potential advantage resulting from the polymer overlayer as the metalized film is protected from direct abrasion. All films prepared with AgHFA displayed excellent adhesion to the polyimide substrate; the metalized layer was unaffected by a variety of adhesive tapes. Mechanical tests for modulus and tensile strength reported in Table 4 show that films maintain very similar mechanical properties after metallization. Thermal analysis in Table 5 shows once again that Tg is not significantly affected by metallization, but thermal decomposition in air (10% weight loss) is lowered due to the catalytic properties of the silver particles.
Figure 3. Reaction to create AgHFA complex in preparation for in situ reduction of silver from Southward 1995. Silver acetate is reacted with HFAH to form AgHFA and acetic acid.

Table 3. Reflectivity as a Function of Concentration for wt% silver as reported in Southward 1995.

<table>
<thead>
<tr>
<th>wt % silver</th>
<th>polymer repeat unit/metal ratio</th>
<th>HFAH/Ag ratio</th>
<th>reflectivity (angle and percent transmittance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>8.7/1</td>
<td>1.2</td>
<td>43 32 12</td>
</tr>
<tr>
<td>5.0</td>
<td>4.3/1</td>
<td>1.2</td>
<td>68 59 33</td>
</tr>
<tr>
<td>7.4</td>
<td>2.8/1</td>
<td>1.1</td>
<td>75 64 46</td>
</tr>
<tr>
<td>9.9</td>
<td>2.0/1</td>
<td>1.1</td>
<td>79 69 49</td>
</tr>
<tr>
<td>12.1</td>
<td>1.6/1</td>
<td>1.2</td>
<td>82 65 52</td>
</tr>
<tr>
<td>17.9</td>
<td>1.0/1</td>
<td>1.1</td>
<td>76 54 36</td>
</tr>
</tbody>
</table>
Table 4. Modulus and tensile strength as a function of wt% silver as reported in Southward 1995.

<table>
<thead>
<tr>
<th>wt % silver</th>
<th>modulus (Ksi)</th>
<th>tensile strength (Ksi)</th>
<th>surface resistivity/volume resistivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>449</td>
<td>21</td>
<td>$6.5 \times 10^{16}$ Ω (air-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$1.5 \times 10^{17}$ Ω (glass-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$9.2 \times 10^{17}$ Ω cm (volume)</td>
</tr>
<tr>
<td>5.0°</td>
<td>497</td>
<td>22</td>
<td>$8.4 \times 10^{16}$ Ω (air-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$7.1 \times 10^{16}$ Ω (glass-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$7.8 \times 10^{16}$ Ω cm (volume)</td>
</tr>
<tr>
<td>7.4°</td>
<td>504</td>
<td>23</td>
<td>$1.7 \times 10^{17}$ Ω (air-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$9.9 \times 10^{16}$ Ω (glass-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$6.8 \times 10^{17}$ Ω cm (volume)</td>
</tr>
<tr>
<td>9.8°</td>
<td>402</td>
<td>17</td>
<td>$6.5 \times 10^{16}$ Ω (air-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$6.7 \times 10^{14}$ Ω (glass-side)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$3.1 \times 10^{17}$ Ω cm (volume)</td>
</tr>
</tbody>
</table>

Table 5. Tg and PDT as a function of wt% silver as reported in Southward 1995.

<table>
<thead>
<tr>
<th>wt % silver</th>
<th>$T_g$ by DSC (°C)</th>
<th>TGA 10 wt % loss in air (°C)</th>
<th>TGA 10 wt % loss in N₂ (°C)</th>
<th>CTE (ppm/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>275</td>
<td>524</td>
<td>540</td>
<td>42.8 \textsuperscript{b}</td>
</tr>
<tr>
<td>2.5</td>
<td>269</td>
<td>361</td>
<td>531</td>
<td>a</td>
</tr>
<tr>
<td>5.0</td>
<td>268</td>
<td>379</td>
<td>489</td>
<td>42.7</td>
</tr>
<tr>
<td>7.4</td>
<td>270</td>
<td>372</td>
<td>488</td>
<td>43.6</td>
</tr>
<tr>
<td>9.9</td>
<td>272</td>
<td>376</td>
<td>491</td>
<td>42.8</td>
</tr>
<tr>
<td>12.1</td>
<td>269</td>
<td>361</td>
<td>531</td>
<td>a</td>
</tr>
<tr>
<td>17.9</td>
<td>272</td>
<td>361</td>
<td>477</td>
<td>a</td>
</tr>
</tbody>
</table>
Several other silver salts were used in Southward’s research to test the effects of ligand choice. The results shown in Table 6 clearly show that ligand choice is critical to forming a highly reflective film with good mechanical properties. Adding hexafluoroacetylacetone (HFAH) to silver acetate (AgOAc) in solution worked the best by a large margin. HFAH-triphenylphosphine (PPh₃) and trifluoroacetic acid (TFAAH) also formed films that were mirrored in appearance, but reflectivity was significantly lower than for the AgHFA films. Trifluoroacetylacetone, (TFAH), TFAH-1,5-COD, and TFAH-PPh₃ also had poor reflectivity, and were greenish and dark in appearance. A few other ligands were tried, but the resulting silver complex did not dissolve in DMAC. The final metalized films from those complexes were heterogeneous and essentially useless.

Table 6. Comparison of various ligands used to metalize BTDA-ODA as reported in Southward 1999.

<table>
<thead>
<tr>
<th>ligand</th>
<th>% reflectivity</th>
<th>X-ray d spacings (Å)</th>
<th>appearance</th>
<th>conductive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(C₆H₄O₂)₂/HFAH</td>
<td>9.9</td>
<td>2.37 (100), 2.03 (20), 1.45 (14), 1.23 (12)</td>
<td>bright metallic/pewter</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/HFAH-PPh₃</td>
<td>8.2</td>
<td>2.34 (100), 2.03 (23), 1.44 (8), 1.26 (6)</td>
<td>brown metallic/pewter</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAAH</td>
<td>7.1</td>
<td>4.41 (16), 2.36 (100), 2.04 (16), 1.47 (14), 1.23 (9)</td>
<td>bright metallic/pewter</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH</td>
<td>8.3</td>
<td>2.34 (100), 2.02 (17), 1.44 (8), 1.23 (9)</td>
<td>metallic green/dark</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH-1,5-COD</td>
<td>8.4</td>
<td>2.36 (100), 2.03 (13), 1.44 (7), 1.23 (7)</td>
<td>metallic green/dark</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH-PPh₃</td>
<td>8.3</td>
<td>2.36 (100), 2.05 (15), 1.44 (8), 1.23 (7)</td>
<td>metallic green/dark</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH-1,5-COD with sinter 300 °C</td>
<td></td>
<td>2.35 (100), 2.04 (19), 1.44 (11), 1.23 (5)</td>
<td>metallic green/dark</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH-1,5-COD with sinter 500 °C</td>
<td></td>
<td>2.34 (100), 2.03 (16), 1.44 (7), 1.23 (6)</td>
<td>heterogeneous</td>
<td>no</td>
</tr>
<tr>
<td>Ag(C₆H₄O₂)₂/TFAH-1,5-COD with sinter 700 °C</td>
<td></td>
<td>2.36 (100), 2.04 (16), 1.44 (7), 1.23 (7)</td>
<td>heterogeneous</td>
<td>no</td>
</tr>
</tbody>
</table>

* Solubilizing ligand abbreviations: TFAAH = trifluoroacetic acid; TFAH = 1,1,1-trifluoroacetylacetone; DBM = dibenzoylmethane; COD = 1,5-cyclooctadiene; PPh₃ = triphenylphosphine. * Peaks are very broad and of low intensity relative to the amorphous polymer halo.

8.7
A later paper from Southward et al.\(^8\) reported the first major success in creating conductive films. BTDA-ODA was doped with AgTFA, AgHFA, and AgTFAA via the in-situ method and then metalized thermally. Previous work on those films used a cure cycle of 100 °C for 1h, 100-300 °C over 3h, and 300 °C for 1h. The results from that original cure cycle (Table 6) showed that AgHFA films cured for that length of time were about 30% more reflective than the AgTFA films. AgTFAA films fell roughly in the middle. Extending the thermal cure cycle (100 °C for 1h, 100-300 °C over 6h, and 3h at 300 °C) revealed an interesting phenomenon shown in Figure 4. AgHFA and AgTFAA films attained their max reflectivity of about 80% just before reaching 300°C. AgTFA films at the same point in the cure cycle were minimally reflective and remained that way until after about 1h at 300°C. After that point, reflectivity rapidly increased to over 90%. AgTFA films also became consistently conductive after a few hours at 300°C. It is not surprising that AgHFA films metalize faster.\(^9\) The only structural difference between TFAH and HFAH is that HFAH has two trifluoromethyl (CF\(_3\)) groups and TFAH has one CF\(_3\) and one methyl (CH\(_3\))[Figure 1]. The extra CF\(_3\) group in AgHFA makes the ligand more electron withdrawing and thus more willing to accept an electron from a reducing agent.

The catalytic properties of nanometer-sized silver metal particles offer a reasonable explanation for why AgTFA films eventually become conductive. X-ray photoelectron (XPS) data in Figure 5 and transmission electron microscopy (TEM) in Figure 6 show that particles of reduced silver were forming in AgTFA films even during the earlier stages of the cure (approx 275 °C), but that these particles were mostly less
that 5 nm in diameter. This was too small to contribute to significant reflectivity. The high effective surface area from the smaller particles promoted a controlled oxidative degradation of the surface layer of the polyimide. The end result was a metalized film where the top polyimide layer observed in earlier films was mostly removed allowing the silver layer to lie on the film’s surface. This explanation is supported by the fact that thermally curing AgTFA-doped films in a nitrogen atmosphere instead of air didn’t form conductive films. Evidence that the top polymer layer was indeed absent was clear in the absence of angular dependence on reflectivity shown in Table 7. Despite partial degradation of the film, Tg and tensile strength were largely unaffected indicating that the oxidative degradation had minimal effect on the film’s mechanical properties. Also, the lack of a protective overlayer did not adversely affect adhesion of the silver layer as tested according to the ASTM adhesion testing protocol. This modification is effective, but still not ideal as it requires high temperature and involves degrading a portion of the film. Is also requires a relatively large amount of silver to achieve reflectivity, much of which remains in the bulk of the polymer (Figure 6) and is thus wasted.

Table 7. Reflectivity, Thermal, and Resistivity Data for (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)-BTDA/ODA films cured to 300 °C for 7 h as reported in Southward 1999.

<table>
<thead>
<tr>
<th>film</th>
<th>% silver (final)</th>
<th>20°</th>
<th>30°</th>
<th>45°</th>
<th>55°</th>
<th>70°</th>
<th>Tg (DSC)</th>
<th>CTE (approx K)</th>
<th>surface resistivity (polished film)</th>
<th>tensile modulus (Ksi)</th>
<th>tensile strength (Ksi)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>275</td>
<td>42.8</td>
<td></td>
<td></td>
<td></td>
<td>7 x 10^5 [at], 2 x 10^3 [glass]</td>
<td>19.7</td>
<td>2012</td>
<td>456</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>13.0</td>
<td>95</td>
<td>97</td>
<td>97</td>
<td>95</td>
<td>91</td>
<td>276</td>
<td>34.3 &lt;0.1</td>
<td>19.7</td>
<td>474</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>12.8</td>
<td>95</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>92</td>
<td>279</td>
<td>33.0 &lt;0.1</td>
<td>20.2</td>
<td>468</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12.8</td>
<td>95</td>
<td>94</td>
<td>92</td>
<td>91</td>
<td>91</td>
<td>273</td>
<td>22.8 &lt;0.1</td>
<td>19.3</td>
<td>445</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated for the AgTFA system decomposing to silver metal and volatile components which are lost from the film. *Reflectivity data are relative to a Perkin-Elmer polished aluminum optical mirror set at 100%. *Four-point probe.
Figure 4. Development of reflectivity as a function of temperature/time for 13% silver(0) BTDA/4,4-ODA films as reported in Southward 1999. The silver(I) precursors are: AgTFAA O, AgHFA □, and AgTFA ▼. Time zero is after holding the film 135 °C for 1 h; from 135 to 300 °C the temperature increase remains constant.
Figure 5. X-ray diffraction patterns in the silver 111 and 200 region for 10.7% AgTFA-BTDA/ODA as reported in Southward 1999. Samples were withdrawn from the oven at the temperatures which are listed at the left of each curve.
Figure 6. Transmission electron micrographs from Southward 1999 (cross sections from the metalized air-side surface down into the bulk of the film) of 10.7% AgTFA-BTDA/ODA films at different cure stages: (A) cured to 275 °C for 0 h; (B) cured to 300 °C for 0 h; (C) cured to 300 °C for 5 h. Films A and B are not conductive; film C has a sheet resistance of 5-15 Ω/sq.

Instead of continuing to focus on the effects of different ligands, later reports analyzed the effects of different polymers. Thompson et al. reported on metalizing ODPA-4,4'-ODA with AgHFA and AgTFA. The results largely mirrored those for BTDA-ODA. AgTFA films took longer cure times to become reflective, but ultimately reached the highest reflectivity and were the only films to become conductive.

All polyimides mentioned up to this point are only soluble as amic acids and are often referred to as traditional polyimides. Selectively fluorinated polyimides are different in that they are soluble in their final imide form as well as the amic acid form. This opens up the possibility of doping a film when it is in the final useable polyimide form, but before any thermal curing. Unfortunately, doping the polyimide form is of
minimal use as it produces films with lower reflectivity [Figure 8]. A significant advantage to some fluorinated polyimides is that they do not absorb light in the visible spectrum. This property is desirable because it has the potential to enhance reflectivity in films with a thin polymer overlay (all films except for those prepared with AgTFA). Davis 2007\textsuperscript{11} reports a comparison study between classical polyimides BPDA/4,4'-ODA and BTDA/4,4'-ODA; and fluorinated polyimides /4-BDAF and 6FDA/1,3,(3)-APB) [Figure 7]. The main discovery was that fluorinated polymers became reflective at lower silver concentrations. This is clearly of interest as less silver means less waste and cost associated with the process.
Figure 7. Significant polymers and chemicals studied in Davis 2007. Left column: polyimide repeat unit structures derived from imidization of the poly(amic acid) precursor. Right column: structures of silver complexes used in polyimide metallization.
Figure 8. Comparisons between poly(amic acid) and polyimide as the starting polymer as reported in Davis 2007. Reflectivity versus time/temperature data for 2.0% Ag films prepared with the poly(amic acid) (○) and polyimide (●) forms of 6FDA/4-BDAF films and the poly(amic acid) (△) and polyimide (▲) forms of 6FDA/1,3(3)-APB films prepared with silver acetate, hexafluoroacetacetone and 6FDA/4-BDAF poly(amic acid) in DMAc.
As shown previously, traditional polyimides typically need >10% Ag by weight to create a highly reflective film even in effective systems such as AgTFA in BTDA-ODA. Figure 9 shows two interesting facts: 1) increasing silver from 8% to 10% actually decreases reflectivity; 2) both 6% and 8% silver films reach a maximum reflectivity of approximately the same value and only maintain that reflectivity for a narrow curing window near 275 °C. The real surprise is shown in [Figure 10] which features films with low silver concentrations. Films with silver weight percents as low as 2% were still nearly 80% reflective in their window of best cure time. After that window, the films with 2-3% Ag retained modest reflectivity, and lost reflectivity with increasing cure times slower than films with high silver concentrations. [Figure 11] shows a direct comparison between traditional and fluorinated polymers at 2% silver. 6FDA/4-BDAF clearly displayed excellent reflectivity performance at low silver concentrations.
Figure 9. Specular reflectivity versus time/temperature data for higher concentration silver-6FDA/4-BDAF films prepared with silver acetate, hexafluoroacetylacetone, and 6FDA/4-BDAF poly(amic acid) in DMAc. The thermal cure cycle is: 20 min to 135°C, hold for 60 min (this is time zero on the reflectivity plots); 135 to 300°C over 240 min; hold constant at 300°C. From Davis 2007.
Figure 10. Specular reflectivity versus time/temperature data for lower concentration silver-6FDA/4-BDAF films prepared with silver acetate, hexafluoroacetylacetone and 6FDA/4-BDAF poly(amic acid) in DMAc. From Davis 2007.

25
Figure 11. Comparison of metallized films derived from fluorinated polyimides, 6FDA/4-BDAF (●) and 6FDA/1,3(3)-APB (▼), with those derived from traditional polyimides, BTDA/4,4'-ODA (◇), BPDA/4,4'-ODA (◇) and ODPA/1,3(3)-APB (△), at 2.0% silver prepared with silver acetate, hexafluoroacetylacetone and the respective poly(amic acid)s in DMAc. From Davis 2007\textsuperscript{11}. 
There are two noteworthy drawbacks to using fluorinated polyimides: First, films reach high reflectivity between 275 °C and 300 °C, but then rapidly lose reflectivity with further heating. Traditional polyimides exhibit a similar behavior, but to a much lesser degree. Second, none of the fluorinated polymers became conductive even if doped with AgTFA for reasons that are unclear. It is of interest to see what happens when a polymer has both fluorinated and traditional elements. Ideally, the end product would feature the best properties of each with high reflectivity at low concentrations of silver, a wide curing window, and conductivity at some point in the curing process. This thesis reports on such a mixed system.

**Experimental**

**Materials.** BTDA was obtained from Wakayama Seika Kogyo Co., Ltd. via Kennedy and Klim, Incorporated. 4-BDAF was purchased from Chriskev (Leawood, KS, USA). BTDA and 4-BDAF solids were dried under vacuum at 150 °C overnight prior to use. HFAH, TFAH, silver(I) acetate (99.9%), DMAC (HPLC grade) and pyridine (99.8% anhydrous) were purchased from Sigma-Aldrich and used as received except for the liquids which were stored in the presence of 4 Å molecular sieves.

**Preparation of Metalized BTDA/4-BDAF Films.** 17% BTDA/4-BDAF in DMAC was prepared by first massing 4-BDAF into a bottle and suspending in DMAC. BTDA was then added to the 4-BDAF/DMAC mixture and stirred thoroughly for several hours. BTDA and 4-BDAF were used in a 1:1 mole ratio and the amount of DMAC was such that the final resin would have 17 w/w% polymer. The BTDA/4-BDAF resin was stored in a refrigerator
with a parafilm seal. 17% BTDA/ODA was prepared via the same steps, but substituting ODA for 4-BDAF as the diamine. BTDA/ODA was used as an adhesion aid for preparing BTDA/4-BDAF films metalized with AgHFA.

Silver acetate (AgOAc) was massed into a small test tube and suspended in a small amount (~1g) of DMAC solvent. HFAH or TFAH was added in a 1:1.1 mole ratio, and the mixture was stirred until all solids dissolved indicating complete conversion of silver acetate to AgHFA or AgTFA. One extra step was used for preparing AgTFA: Pyridine was added to the AgOAc/DMAC/TFAH mixture in a 2:1 mole ratio relative to silver acetate to promote the reaction. Silver acetate isn’t soluble in DMAC while AgHFA and AgTFA are, providing a useful visual indication of complete reaction. The solution of AgHFA or AgTFA in DMAC was added to BTDA/4-BDAF resin immediately after mixing without any steps taken to isolate the silver salt. The test tube containing the silver solution was rinsed with 2 small aliquots (~1 mL) of DMAC both of which were transferred to the resin. This step was performed to ensure complete transfer of silver to the BTDA/4-BDAF resin. The desired percent of silver in the final film was manipulated by adjusting the amount of silver acetate and HFAH/TFAH used. The amount of resin used was kept constant. Silver doped resin was then cast into a single ca. 4.5 mm thick film on adjacent 27 x 46mm petrographic slides and dried in a drying box with slowly flowing dry air for at least 12 h. The slides were separated before drying to facilitate handling them later. Slides with an incomplete film layer were discarded. Curing was performed in a GS Blue M oven with the intake vent closed. The films were
subjected to the following thermal cycle: 20 min. to 135 °C, hold at 135 °C for 1 h, 4 h to 300 °C, hold at 300 °C for 5 h. Samples were removed from the oven for analysis every 25 degrees up to 300 °C, then every hour for the next 5 h.

Films metalized with AgHFA displayed poor adhesion to the petrographic slides. This caused the films to separate from the slide during the curing process and create an uneven surface inappropriate for reflectivity measurements. This issue was solved by applying the AgHFA-doped BTDA/4-BDAF to a BTDA/ODA substrate instead of the bare petrographic slides for samples that were intended for reflectivity characterization. Specifically, several adjacent petrographic slides were coated with a ca. 4.5 mm thick film of BTDA/ODA, separated, and dried in the dry box overnight. The dried BTDA/ODA-coated slides were thermally imidized at 300 °C. Unevenly coated slides were once again discarded. The Ag doped BTDA/4-BDAF film was then cast onto the BTDA/ODA coated petrographic slides and cured via the same procedure used for all the other films.

**Characterization.** SEM micrographs were obtained using a Hitachi S-4700 field emission SEM. Non-conductive samples were coated with 5-10 nm of Pd/Au alloy. TEM micrographs were obtained on a Jeol JEM-2100F TEM. Specular reflectivity data was measured using a Perkin-Elmer Lambda 35 UV/VIS spectrophotometer equipped with a variable angle specular reflectance attachment. The spectrophotometer was standardized with a Perkin-Elmer polished aluminum mirror (reflectivity coefficient of 0.92 at 531 nm) and all measurements were taken at 531 nm. Glass transitions temperatures were measured on films in sealed pans using a Seiko DSC 210 at a heating
rate of 20°C/min. Thermogravimetric analysis was performed with a TA Instruments TGA Q500 under both flowing air and nitrogen (50 mL/min) at a heating rate of 2.5 °C/min. X-RAY diffraction data was obtained on a Bruker SMART APEX II (4K CCD System with 3-circle goniometer). Two point surface resistivities were measured with a FLUKE 111 digital multimeter.

Results and Discussion

Synthesis and General Appearance of Metalized Films. The procedure used to metalize BTDA/4-BDAF films is illustrated in Figure 1 and described in detail in the Experimental section. Using silver acetate (AgOAc) to synthesize the silver complexes AgHFA and AgTFA and using those complexes immediately to dope BTDA/4-BDAF without isolation is a key step in forming polyimide films with high reflectivity. Formation of the silver complexes can be verified visually without isolating them. AgOAc is insoluble in dimethylacetamide (DMAc), while AgHFA and AdTFA are soluble. A complete reaction to silver complex can thus be visually observed when the slurry of AgOAc and HFAH or TFAH in DMAc becomes a homogeneous, pale yellow solution of AgHFA or AgTFA in DMAc. Pyridine is used as an additive for the formation of AgTFA to promote the reaction by facilitating proton transfer. Pyridine also has the effect of reducing the viscosity of the final doped BTDA/4-BDAF resin.

All films metalized with AgHFA displayed poor adhesion to the bare glass petrographic slide substrate. This allowed the films to separate from the substrate
during the curing process and caused the formation of large bubbles or cracks in some cases. In order to create smooth film surfaces and obtain meaningful data, optical measurements were performed on films that were cast on petrographic slides pre-coated with BTDA-ODA. Specifically, undoped BTDA/ODA resin was cast on petrographic slides and allowed to dry overnight. The dried BTDA/ODA layer was thermally imidized at 300 °C. Doped BTDA/4-BDAF resin was then cast on the BTDA/ODA substrate, dried, and thermally cured. The AgHFA films adhered well to the BTDA-ODA substrate which facilitated forming consistent films for analysis. AgTFA films adhered to unmodified glass slides without difficulty, but the BTDA-ODA substrate was still used to prepare films for optical characterization to ensure experimental consistency with data from the AgHFA films.

**General Appearance of Cured Films.** AgHFA films with 2% and 4% silver developed a highly mirrored appearance at about 250 °C and maintained a similar appearance throughout the curing process. Increasing the percentage of silver introduced imperfections in the mirrored appearance such as bubbles, cracking, and cloudiness. AgTFA films were generally less reflective than corresponding AgHFA films. The highest degree of mirror-like appearance of AgTFA films was typically achieved around 300°C which is a higher temperature than that required for AgHFA films. Before that temperature, the films were either yellow or dark. After curing for about 2 hours at 300°C, the films developed a matte silver appearance and in most cases had a powdery layer on the surface that could easily be disturbed by brushing with a finger. As will be
discussed further below, this powder layer was moderately conductive. Other than the
films containing 2% and 4% Ag from AgHFA, BTDA/4-BDAF films metalized with AgHFA
and AgTFA were less consistent and had more defects than previous films from
BTDA/ODA\textsuperscript{8} and 6FDA/4-BDAF\textsuperscript{11}.

\textbf{Figure 12.} Images of metalized BTDA/4-BDAF films at different cure stages: A) 2% AgHFA
cast on BTDA/ODA substrate; B) 4% AgHFA cast on BTDA/ODA substrate; C) 6% AgHFA
cast on BTDA/ODA substrate. The red numbers under sample correspond to the
temperature in °C at which that sample was removed from the oven.
Figure 13. Images of metalized BTDA/4-BDAF films at different cure stages: A) 8% AgHFA cast on BTDA/ODA substrate; B) 13% AgHFA cast on BTDA/ODA substrate; C) 2% AgHFA cast on glass substrate. The red numbers under sample correspond to the temperature in °C at which that sample was removed from the oven.
Figure 14. Images of metalized BTDA/4-BDAF films at different cure stages: A) 4% AgHFA cast on glass substrate; B) 8% AgTFA cast on BTDA/ODA substrate; C) 13% AgHFA cast on glass substrate. The red numbers under sample correspond to the temperature in °C at which that sample was removed from the oven.
Figure 15. Images of metalized BTDA/4-BDAF films at different cure stages: A) 8% AgTFA cast on glass substrate; B) 8% AgTFA cast on glass substrate; C) 13% AgTFA cast on glass substrate. The red numbers under sample correspond to the temperature in °C at which that sample was removed from the oven.
Reflectivity of Metalized Films. Reflectivity data presented in Figure 16 agrees well with casual observation of the films. AgHFA films were most reflective at 2%, 4%, and 6% silver, and reached maximum reflectivity at about 275 °C (200 min in the cure cycle). Max reflectivity in those films was very high, essentially equivalent to that of the calibrating mirror. Increasing silver to 8% and 13% Ag from AgHFA resulted in a progressive decrease in max reflectivity down to about 70% for 13% Ag. Those films also attained their highest reflectivity around 275 °C and 200 min. The high reflectivity at low concentrations of silver is consistent with previous work on 6FDA/4-BDAF by Davis et al. presented in Figure 9 above. This indicates that the hybrid polyimide being analyzed in this project retains at least some of the beneficial properties of pure fluorinated polyimides. Unfortunately, BTDA/4/BDAF suffers from the same drawbacks as 6FDA/4-BDAF; namely a narrow window of high reflectivity in the curing cycle, and declining reflectivity at higher silver concentrations.

AgTFA film reflectivity is charted in Figure 17. Since the AgTFA films could be prepared on both glass and BTDA/ODA substrates, the effect of substrate on reflectivity was tested. Reflectivity of films cast directly on glass was slightly lower. The overall trend was otherwise unaffected indicating that casting films on a BTDA/ODA base instead of a bare petrographic slide causes a minimal degree of deviation in reflectivity. Reflectivity was only tested at 8% and 13% for AgTFA films, and neither set of samples was able to reach more than about 70% reflectivity. Maximum reflectivity was observed when the films first reached 300 °C in the cure cycle. Further curing at 300 °C resulted in
a progressive loss in reflectivity down to almost zero. The 13% film was somewhat lower in maximum reflectivity, but the difference was smaller than between the 8% and 13% AgHFA films. This seems to indicate a lower dependence of reflectivity on percentage of silver in AgTFA films than AgHFA films. Whether that observation is significant or not is unclear at this point. A concept that is clear is that all fluorinated and partially fluorinated polyimides tested thus far suffered a significant loss in reflectivity after a certain point in the cure cycle. The exact temperature and time at which that occurs depends on the specific system being analyzed, but the trend remains the same.
**Figure 16.** Specular reflectivity versus time data for metalized BTDA/4-BDAF films containing 2%, 4%, 6%, 8%, and 13% Ag from AgHFA. All films were cast on BTDA/ODA substrate. The thermal cure cycle was 20 min to 135 °C; hold for 60 min (time zero on the reflectivity plots); 135 °C to 300 °C over 240 min; hold constant at 300 °C.
Figure 17. Specular reflectivity versus time data for metalized BTDA/4-BDAF films containing 8% and 13% Ag from AgTFA. Sample films were cast on both BTDA/ODA and glass substrates to compare results. The thermal cure cycle was 20 min to 135 °C; hold for 60 min (time zero on the reflectivity plots); 135 °C to 300 °C over 240 min; hold constant at 300 °C.
**Conductivity and Film Morphology.** BTDA/4-BDAF films prepared with AgHFA were mostly nonconductive which is not surprising considering the results from metalized BTDA/ODA\(^8\) and 6FDA/4-BDAF\(^{11}\). There is an interesting exception. Several 8% and 13% AgHFA films developed regions with various blue tints. A sample demonstrating this phenomenon is pictured in Figure 18. The innermost of these regions was conductive in the 10-100 ohm range. This is of particular interest as it is the first time to our knowledge that significant conductivity has been observed in a polyimide film metalized by AgHFA. The conductivity is not consistent throughout the films making them useless for practical applications. Nonetheless, this is a system that may warrant further investigation in the future to determine a way to extend the conductive region to the entire film’s surface.

![Figure 18](Image)

**Figure 18.** Close up image of a BTDA/4-BDAF film containing 13% Ag from AgHFA. This sample was cast on a BDIA/ODA substrate and cured for 3h at 300 °C. The conductive regions are indicated by arrows.
13% AgTFA films also gave interesting results for conductivity. Most 8% and 13% AgTFA films cured past 2 hours at 300°C were conductive. There was however no consistency in conductivity. A few samples were highly conductive with a resistance of ca. 1 Ω. Others were barely conductive, giving readings on the order of megaohms and higher. Further analysis revealed that only the silver powder on top of the films were conductive. This layer was easily disturbed by touching with fingers or the voltmeter’s probes, and removing the layer eliminated the conductivity. An example of a film with a disturbed top layer is provided in Error! Reference source not found.. Since the ultimate purpose of a conductive film is to be used in real world applications, a conductive layer that can be destroyed so easily is not desirable. Compared to the BTDA/ODA films metalized with AgTFA in research done by Southward et al \(^8\) which were both highly reflective and consistently conductive, these BTDA/4-BDAF films are inferior in both attributes.

Figure 19. Close up image of a BTDA/4-BDAF film containing 13% Ag from AgTFA. This sample was cast on a glass substrate and cured for 3h at 300 °C. The dark regions are areas where the powder layer has been disturbed by gentle contact with fingers and taking conductivity measurement with the multimeter.
TEM micrographs (Figure 20) of 13% AgTFA films confirm that the top layer of metalized silver is poorly adhered. A key point to remember when analyzing these images is that TEM slide preparation involves embedding the slide in a resin, then cutting to the appropriate thickness with a microtome. The top two images are different samples from the same film cured for 2 hours at 300°C. This film has not developed the powdery layer yet. The images show a relatively smooth layer of silver near the top of the film. The bottom images are from a powder-coated 13% AgTFA film cured for 2 hours at 300°C. These samples have “towers” of silver on top of the film instead of a single smooth layer. A reasonable explanation for these towers is that portions of the silver layer partially separated from the film during the preparation process because of the poor adhesion.

The theory used to explain conductivity and the lack of a polymer overlayer in BTDA/ODA films metalized with AgTFA can be applied here to provide a possible theory for why BTDA/4-BDAF films metalized with AgTFA have a conductive layer of powder on the surface. In the case of BTDA/ODA, it was observed that the curing process involved the formation of silver nanoparticles of ca. 5nm diameter with a high effective surface area. These silver particles were proposed to be responsible for oxidatively degrading the surface overlayer of polyimide. In that case, the surface degradation had the beneficial effect of creating a conductive film and no major
drawbacks. X-Ray diffraction (XRD) and SEM data collected on AgTFA metalized BTDA/4-BDAF films indicates that silver nanoparticles of a similar size are again present. XRD (Figure 21) peaks from 175 °C up to the first sample at 300 ° show broadened peaks. This is an indication of Scherrer broadening caused by nano-scale (~ 5 nm) crystallites of silver. SEM micrographs visually show the presence of nanoparticles under 10 nm diameter until particle aggregation and sintering occur after curing for 1 h at 300 °C. The point at which the particles appear to aggregate in the SEM images corresponds to the first conductive films. Based on that data, it is reasonable to propose that the silver particles present before curing for 2h at 300 °C were sufficiently small to promote oxidative degradation of the films’ top layer just like in the conductive AgTFA – BTDA/ODA films. However, unlike in the BTDA/ODA films, degradation progressed to the point of compromising the integrity of the metalized silver surface. Based on differential scanning calorimetry to determine the glass transition temperature Tg, the bulk of the BTDA/4-BDAF film was not significantly affected by the curing process; only the surface. Tg is essentially the same at ca. 245 °C in both undoped, cured BTDA/4-BDAF and in metalized films with both 8% and 13% Ag from AgTFA.
Figure 20. TEM images of BTDA/4-BDAF metalized with 13% Ag from AgTFA and cured to the following temperatures: (A and B) 300°C-2h; (C and D) 300°C-3h. Images B and D were taken from a film that was cured separately from the film used for images A and B to confirm that the towers were not a fluke.
Figure 21. X Diffraction patterns for 13% AgTFA-BTDA/4-BDAF and 13% AgHFA-BTDA/4-BDAF. All peaks shown are from silver. The numbers at the right of each curve indicate the cure for that sample.
Figure 22. SEM micrographs of BTDA/4-BDAF metalized with 13% Ag from AgTFA and cured to the following temperatures A) 275 °C; B) 300 °C for 1 h; C) 300 °C for 3 h D) 300 °C for 4 h. Images A and B are before the film became conductive, and C and D are after.
Summary of experimental results. BTDA/4-BDAF films metalized with 6% or less Ag from AgHFA became highly reflective at a relatively low temperature, but remained nonconductive throughout the cure cycle. Films metalized with 8% and 13% AgHFA had lower reflectivity, but became conductive in selected regions on the film. AgTFA films never developed a highly reflective surface. Fully cured samples became conductive, but the conductive layer was poorly adhered to the film. These results are interesting, but ultimately lead to the conclusion that metalized BTDA/4BDAF has no significant advantages and two critical disadvantages over films made from either pure classical or pure fluorinated base polyimides. The high reflectivity at relatively low concentrations of silver observed in the AgHFA in BTDA/4-BDAF films can also be obtained from 6FDA/4-BDAF films. BTDA/4-BDAF films metalized with AgTFA are not highly reflective and have unstable conductivity compared to similar films prepared with BTDA/ODA.
Works Cited


Appendix: On a Facile Approach to Silver-Patterned Dielectric Substrates -

Part 2: The Importance of Silver Nanoparticle Size

(Note: this is a draft of a manuscript to be published. A portion of this body of work was finished as a Master’s student)

Introduction

This appendix describes significant enhancements of our initial efforts\(^1\) in preparing silver-patterned films by directly adhering dry silver nanoparticles to an ink-printed design on a dielectric substrate, e.g., glass. Our initial work invoked a ternary “nanometal—binder (the ink of the pattern)—substrate” concept to bind silver nanoparticles selectively to the solvent-free ink that defined a pattern on the surface of a glass or polyimide substrate. Our process allowed for full and continuous substrate coverage or patterned surface arrays. A major appeal of the process lay in its simplicity and rapidity. The desired pattern was drawn with a permanent ink marking pen. A dry silver nanopowder (average diameter ca. 120 nm) was then applied by direct contact to the solvent-free inked substrate using only minimal pressure. Interestingly, the nanoparticles adhered only to the ink residue; they were easily brushed free from the non-inked dielectric base. Subsequent heating to a maximum temperature 300 °C led to silver nanoparticle sintering with a concomitant increase in conductivity only to within two orders of magnitude of bulk polycrystalline silver.
Major aspects of the present investigation center on lowering the sintering/processing temperature and achieving a more optimal electrical conductivity. Toward these ends we report a new and reliable synthetic route to smaller silver nanoparticles (predominately 5-10 nm in diameter) than previously used (ca. 120 nm) and the subsequent use of these smaller nanoparticles to form metalized patterns. The larger surface area to volume ratio of the smaller nanoparticles allow for lower sintering temperatures and also greater adhesion to the inked pattern.

**Experimental**

**Materials.** Fine and Extra Fine Sanford Sharpie® Permanent Ink Markers and 3M transparent adhesive tape were purchased locally. Silver acetate (AgOAc, 99.99%), dodecylamine (98%) and phenylhydrazine (97%) were purchased and used as received from Sigma-Aldrich (St. Louis, MO). Methanol, toluene, and acetone, all reagent grade, were obtained from Fisher Scientific (Fair Lawn, NJ). Hexafluoroacetylacetone (HFAH) was refrigerated and used as received from Sigma-Aldrich (Ward Hill, MA). Commercial Kapton film was a gift of R. L. Kiefer. Glass petrographic slides (27x46 mm) were obtained from Buehler Ltd. (Lake Bluff, IL).

**Synthesis of silver nanoparticles.** In a typical experiment, hexafluoroacetylacetonato)silver(I) (AgHFA) was prepared without isolation by stirring 0.167 g (1 mmol) of AgOAc into 2 mL of toluene in a vial to form a slurry and then adding 0.229 g (1.1 mmol) of HFAH. Once the solution was completely clear,
complexation was assumed to be complete, as reported by Southward and Thompson using dimethylacetamide as the solvent.²

The AgHFA solution was then used to replace AgOAc in the method of Ong and coworkers,³ along with the following modifications. Into a 100-mL round-bottomed flask having a Teflon*-coated magnetic stir bar, we weighed 1.853 g (10 mmol) of dodecylamine, along with 38 mL of toluene. The AgHFA toluene solution was then added to the reaction flask, and the flask lowered into a 60 °C oil bath. A homogeneous solution resulted.

A solution of 0.038 g (0.33 mmol) of phenylhydrazine in 10 mL of toluene was added slowly to the stirring solution in the reaction flask via a syringe pump over 5 min during which the solution turned light yellow, tan, brown, and then dark brown sequentially over ca. two minutes, indicative of silver(I) reduction with the formation of nanoparticles, the yellow color arising from the plasmon resonance at ca. 420 nm associated with silver nanoparticles. The reaction was allowed to proceed at 60 °C for 30 min after phenylhydrazine addition was complete, at which point the reaction flask was removed from the bath and allowed to cool to room temperature.

Once the reaction had cooled, 10 mL of acetone was added to inactivate remaining phenylhydrazine. Acetone and toluene were then removed from the flask by rotary evaporation at 50 °C. The remaining dark solution was added to 100 mL of a stirring 50 % (v/v) solution of methanol and acetone to precipitate the silver nanoparticles. The particles were allowed to settle for 2 h. The optically clear
supernatant was then decanted and discarded. A fresh 50 mL of acetone were added to the beaker containing the particles for a second wash. The particles were again allowed to settle for 2 h, and the optically clear supernatant was again decanted and discarded. The remaining solid was left to dry in air, yielding a dark powder. Centrifugation was observed to promote irreversible aggregation of the silver nanoparticles, and was not used to accelerate particle settling.

**Pattern metallization and post-fabrication enhancement of conductivity.** Substrates intended for full-surface metallization or for patterned metallization were prepared as described in our previous paper. To metallize the entire surface of a 27 mm x 46 mm petrographic slide for characterization purposes, it was coated with Sanford Sharpie® permanent marking ink by drawing overlapping lines parallel with the short (27 mm) dimension of the slide. The slide was allowed to dry at room temperature for several minutes. Alternatively, any desired pattern could be drawn on a substrate with the permanent ink pen, with a resolution of ca. 300 microns. Substrates which allow for complete selectivity include glass, polyimides (Kapton and Ultem), silicon wafers, epoxy circuit board substrates, stainless steel, polyethylene terephthalate, and polyethylene.

Silver nanoparticles were placed onto a dry inked pattern and then gently wiped across the entire surface with a piece of latex glove. The nanoparticles readily adhered to the inked pattern with minimal pressure. Regardless of pressure, they did not adhere to the un-inked portions of the substrate. Several (usually three to five) passes would
leave the surface fully metallized and conductive. Unbound nanoparticles were collected and recycled as scanning electron microscopy indicated no deformation of the particles during the application process (see Figure 1). Subsequent to fabrication and initial characterization of the metal surface, one of two procedures to enhance conductivity were taken. In the first post-procedure, the silver surface was polished with a non-abrasive material such as a silver polishing cloth. In the second post-procedure, the substrate and surface were thermally annealed in a GS Blue M forced-air oven (Series 146 with Pro-350 controller).

**Characterization.** Two-point resistance measurements were made with a FLUKE 111 digital multi-meter and a TENMA 72-2035 digital multi-meter. Sheet resistivity measurements were taken with a Lucas Signatone SYS-301 four-point probe. Scanning electron microscopy was performed with an Hitachi S-4700 field emission SEM. Thermogravimetric analysis was performed using a TA Instruments Q500 TGA. Scotch-tape tests for adhesion (ASTM D3359-08) were performed with a transparent adhesive from 3M; the classification scheme for results was the same as previously reported by us.¹

**Results and Discussion**

**Synthesis of silver nanoparticles.** In our hands the silver nanoparticle synthetic protocol described by Li, Wu, and Ong³ yielded particles larger than those (“sub-10 nm”) reported. (See Figure 1S in Supplementary Material.) In our judgment this simply points to the too seldom acknowledged difficulty of exactly reproducing silver nanoparticle
syntheses from group to group due to modest changes in reagent source and purity, reaction conditions, and surreptitious impurity levels. Indeed, Li, Wu, and Ong in a subsequent publication,4 allude to the fact that consistent results in the synthesis of silver nanoparticles is not a simple matter. They note,

“...the preparation of such silver nanoparticles for low-temperature coalescence to conductive elements remains relatively challenging synthetically. The low yields or poor stability of silver nanoparticles may lead to increased cost and potentially preclude their adoption in practical applications.”4

A most convincing and disturbing case for the difficulties in silver nanoparticle reproducibility is found in the silver nanowire work of Xia and coworkers. After initial and impressive reports of nanowire syntheses5-7 that mentioned no difficulties, it was latter acknowledged that impurities or added components such as oxygen gas, chloride ions, metals, or metal ions can drastically alter the resultant nanoproducts obtained.8-15 Nonetheless, we found the Ong et al. synthetic procedure with small modifications very helpful. The following allowed us to readily synthesize significantly monodisperse, quasi-spherical particles predominantly in the 5-10 nm regime (determined by scanning electron microscopy), with a modest 1.5 wt % dodecylamine (determined by TGA – see Figure 2 SI) coupled to the metal nanoparticles..
While Ong and coworkers indicate a much higher weight percent coating—22 wt % by TGA for oleylamine-stabilized particles our 1.5 wt % is not unreasonable for the following reasons. 1. amines not competitive with thiols; 2. easily washed away; and 3. ready sintering. Furthermore, the affinity of silver for nitrogen donor atoms is considerably less than sulfur for silver or gold\textsuperscript{16} as a result, the ca. 1.5% coating we report seems reasonable. The low amine fraction is helpful in giving a purer silvered pattern as less organic material has to be lost from the pattern upon heating.

Instead of beginning with insoluble silver acetate,\textsuperscript{3} we began with the stable and toluene soluble (hexafluoroacetylacetonato)silver(I) complex (AgHFA). We also diminished the concentration of reducing agent by a factor of three, to slow the reduction rate, and we halved the reaction time, to prevent excessive Ostwald-like ripening. In addition, we eliminated centrifugation from the purification steps, as we found it caused our particles to aggregate irreversibly. This may be due to the low amine coverage. The size distribution determined from SEM images resulting from the modified procedure was: 22% ≤5 nm, 72% 6-10 nm, 6% 11-20 nm, and 1% ≥21 nm. See Figure 1.

**Metallization and post-fabrication enhancement of properties.** Mass versus time studies showed that nearly all solvent that could evolve from the inked pattern has done so within two minutes at room temperature. The pattern is tack-free within a minute, and completely dry within two. At least five minutes were generally allowed; after the ink was dry no difference in adhesion was observed as a function of time.
As we previously observed, application of amine-protected silver nanoparticles was facile and selective. The particles adhered only to the dry ink pattern, with no particle deformation resulting from the application process, as shown in the SEMs of 2A,B. Modification by buffing or polishing was readily accomplished. This process does result in a deformation of the nanoparticles, shown in Figure 2C. It is reasonable to believe that the slight increase (see Table 1) in sheet resistivity, symbol $\rho_s$ below, resultant from this process actually represents a decrease—or at least no change—in bulk resistivity, $\rho_b$, as:

$$\rho_b = \rho_s \cdot t \quad (1)$$

and the buffing likely compresses the malleable silver layer, decreasing its thickness, $t$.

Modification by heating also proved straightforward. Samples were removed from the oven once the temperature reached the value indicated in Table 1.

**Conductivity.** As shown in Table 1, the samples are generally rather conductive upon application of the nanopowder to the ink pattern. Subsequent modification by heating results in an overall decrease in resistivity, converging on 0.03 ohms/square (the approximate limit of detection of our instrument). Exploration of this phenomenon by SEM indicates that this is due to sintering of the initial nanoparticles into larger
particles, and ultimately, a continuous network of silver (see Figure 3). It is important to note that the sintering begins at much lower temperatures, and proceeds more quickly, than we reported previously for much larger nanoparticles. Sintering commences at or before 50 °C, and is effectively complete by 125 °C (sintering still occurs after this temperature, as shown in Figure 3, but it does not enhance the electrical conductivity; one might expect an increase in the maximum current density, though this was not probed). In our previous paper, sintering did not begin before ca. 150 °C, and was not complete before ca. 300 °C. Additionally, the previous resistivities were often higher than presently observed, even after thermal treatment to 300 °C. Clearly, beginning with smaller silver nanoparticles is beneficial.

As described in equation (1), the product of the sheet resistivity and the thickness is the bulk resistivity of a three-dimensional sheet. By scanning electron microscopy, we were able to determine the approximate thickness of the silver layer adhered to the ink pattern. We performed SEM on a boron-doped silicon wafer with ink and nanoparticles applied as described, broken in half and turned such that the incident electron beam was parallel to the silver layer, that is, perpendicular to the cross-section. The images (Figure 4) indicate that the surface silver layer is approximately 1-2 microns in thickness. This sample was not thermally treated, meaning that this represents the upper limit on the possible thickness of the final sintered layer. Taking an average value of 1.3 microns in thickness, the bulk resistivity would be $3.9 \times 10^{-8} \Omega \cdot m$, which would then be an upper limit on the resistivity of the heated samples. Thus, this process provides
resistivities well within one order of magnitude of that of bulk polycrystalline silver, at $1.6 \times 10^{-8} \, \Omega \cdot m$, and likely within a factor of two thereof. This represents a conductivity improvement by at least a factor of 10 over our results reported previously.

**Adhesion.** The adhesion of the silver layer to the ink pattern was measured using the Scotch Tape Test (ASTM D3359-08), with a transparent adhesive from 3M. The standards used are described in our previous paper, and can be summarized as follows: 3M Scotch Tape® is applied to the silvered surface, pressed down firmly, and then peeled off. “Zero” adhesion is demonstrated when all of the metal comes off with the tape. “Poor” adhesion is demonstrated when a large amount of the silver comes off with the tape, interrupting the conductivity of the surface. “Fair” adhesion is demonstrated when a moderate amount of silver comes off with the tape, visually disturbing the surface, but not interrupting conductivity. “Good” adhesion is demonstrated when only a superficial amount of silver comes off with the tape. “Excellent” adhesion is demonstrated when no silver comes off. Tape can be applied in the primary direction of application (longitudinally), or perpendicular to that direction (transversely). Adhesion data are tabulated in Table 2. As shown, heating provides generally superior adhesion. However, the process has enough variability that perfect replication from sample to sample was not realized.

The adhesion of the amine-coated nanoparticles was generally superior to that of the larger particles previously reported. If one assigns values between 0 (poor) and 4
To the adhesion ratings tabulated, the average adhesion we reported previously\textsuperscript{1} was 1.5 for polished samples, and 2.1 for heated samples. We now report average adhesions of 2.0 for polished samples, and 3.2 for heated samples. Thus, the process reported herein provides substantially improved adhesion.

**Conclusion**

We set out to explore further the adhesion of silver nanoparticles to glass and polyimide substrates via a polymeric ink binding layer. In so doing, we utilized nanoparticles narrowly distributed around 5-10 nm in diameter, postulating that this would lead to higher adhesion and lower sintering temperatures, because of the very high surface area to volume ratio and high surface free energy of these small nanoparticles. Both predictions were experimentally realized, with excellent adhesion in many systems, and a maximum necessary sintering temperature of 125 °C. Rapidly heating the samples to this temperature yielded resistivities consistently on the order of that of bulk polycrystalline silver.

**Acknowledgements**

The authors are grateful to the Virginia Space Grant Consortium and the Jeffress Memorial Trust for partial support of this work.
References


Figures for the manuscript.

Figure 1. Size distribution of silver nanoparticles prepared with (hexafluoroacetylacetonato)silver(I) in the modified Li, Wu, and Ong\textsuperscript{3} procedure determined from scanning electron microscopy.
Figure 2 Scanning electron microscope images at high magnification (ca. 200,000X) of purified silver nanoparticles: (A, left) dropped onto copper tape on a SEM stub, (B, middle) after application to dried Sanford permanent ink, and (C, right) after application to dried Sanford permanent ink, with subsequent buffing. The scale bar (20 nm) applies to all images.
Figure 3. Scanning electron microscope images at high magnification (100,000x) of the silvered surfaces after heating in a temperature series. Significant sintering clearly occurs below 100 °C, and the process continues through 300 °C. The scale bar (100 nm) applies to all images.
Figure 4. Cross-sectional scanning electron microscope image at 25,000x magnification. Scale bar represents 1 micron; labeled distances are the minimum and maximum thickness of the silver layer.
Tables for the manuscript.

Table 1. Sheet resistivity of silvered surfaces as a function of post-fabrication modification. Entire inked petrographic slide was embossed with silver nanoparticles at 22 °C and then either polished and heated in a post-treatment.

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<th>As applied</th>
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<th>Heated</th>
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Table 2. Adhesion of silvered surfaces as a function of post-fabrication modification.

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