PLASMA ENHANCED CHEMICAL VAPOR DEPOSITION
OF
THIN ALUMINUM OXIDE FILMS,

A Thesis Presented to
The faculty of the College of Engineering and Technology
Ohio University

In Partial Fulfillment
of the Requirements for the Degree
Masters of Science

by
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1.0 INTRODUCTION

Polyimide composite materials, (PMCs), because of their strength and low mass, are being used in a wide array of applications replacing metals. The use of PMCs in aerospace applications is receiving increased attention because their mechanical properties exceed those of many conventional materials currently being used. The weight savings are driving designers to incorporate PMCs into aircraft design.

PMCs currently comprise 4% of commercial aircraft and 10% of military aircraft by weight. Polyimide composites have also found extensive applications in space exploration. For example, Dupont Kapton® will be used as the solar cell mount for Space Station Freedom.

To realize more widespread application of PMCs, the high temperature performance must be extended. This requires improving the thermal oxidation stability. Currently the maximum service temperature of PMCs is about 370 °C. At higher temperatures in an ambient air environment, PMCs undergo oxidative degradation, rendering them useless as structural materials. Experimental evidence confirms the detrimental effect of oxygen on PMCs. The PMC will not survive, due to thermal oxidative degradation, 100 hours at 425 °C in an oxygen environment. After 600 hours in a nitrogen environment at 425 °C, the PMC will retain its strength despite a weight loss of 10 percent.
Coatings can be applied to PMCs so as to avoid the volatization and delinking of the molecule chains and to retain the mechanical properties. Such a coating excludes oxygen from contacting and reacting with the polymer. Three primary factors in the viability of a protective coating are (Ref 1):

- The relatively low temperature tolerance of PMC's require that the coating application takes place at less than 450 °C.

- The coating must have excellent adhesion at elevated temperatures, be resistant to thermal cycling, wear, and acoustical vibration.

- The coating must possess the morphology and microstructure to limit oxygen diffusion (as well as atomic-oxygen bombardment-induced damage, if it is to be used in low earth orbit).

In general, ceramic materials are highly oxidation resistant, and they have been successfully applied as oxidation resistant coating to metals, other ceramics, and carbon-carbon composites.

Chemical vapor deposition is a method to apply thin protective coatings on composite surfaces. The primary advantages of CVD are its ability to prepare a large variety of coatings and to provide coverage of rough or irregular
surfaces. Plasma enhanced CVD allows for deposition at lower temperatures. CVD has been used to apply ceramic coatings to polyimide composites (Ref1).
2.0 LITERATURE REVIEW

2.1 Use of ceramics to coat polyimide composites to increase high temperature use

Harding (Ref1) at NASA's Lewis Research Center coated polyimide composites with aluminum oxide films to improve their high temperature performance. Coatings were made by two methods. The first was physical vapor deposition, where a magnetron sputtering system was used at temperatures of less than 300 °C. The second method he used was metal organic chemical vapor deposition (MOCVD) of aluminum oxide from aluminum tri-isopropoxide.

In the MOCVD process, processing conditions that favored rapid film growth, which were low flow rates and high concentrations, all resulted in a powdery, fragile, and poorly adhering aluminum oxide film. Process conditions that gave slow growth rates (less than 170 Å/min), which were low precursor concentrations and high gas flow rates, produced a coating that appeared to be amorphous and continuous.

Polyimide samples were coated and tested for oxidation durability. This involved heating the coated polyimide along with blank samples in a furnace for 200-300 hours at temperatures of 316-343 °C. Results showed a 25-40 % improvement (reduction in the percent mass loss from original mass) for the aluminum oxide coated samples compared to the uncoated samples. He concluded that the value of the coating
appears to be in the quality of the film deposited, not in the thickness of the film.

Neogi (Ref2, Ref3) has coated polyimide composites with silicon dioxide thin films of 500-5000 Å thickness. His method of deposition was a pyrolytic, plasma-induced decomposition of tetraethylorthosilicate at the heated surface of the composite in a CVD system. Films were made at 275-400 °C under the influence of a radio frequency discharge of 13.56 MHz. Properties of the film, such as refractive index, density, stress, stoichiometry, and adhesion were obtained as a function of process parameters including temperature, pressure, and RF power. He used deposition rates of 80-215 Å/min. He found that thinner films (less than 1000 Å) adhered better than thicker films. To improve adhesion, some of the films were ion implanted with He\textsuperscript{2+} at various energy levels. In all cases, when the polyimide samples coated with silicon dioxide films were tested for high temperature durability by placing the samples in an oven at temperature of 317-390 °C, reduction in weight loss was achieved versus an uncoated sample.

2.2 Preparation of aluminum oxide films

Aluminum oxide films have been prepared by various methods. Aluminum oxide coatings are widely used in the
electronics industry as insulators. In many instances, silicon or some other semiconductor is used as the substrate.

In 1964, Aboaf (Ref 4) deposited aluminum oxide films by the thermal decomposition of aluminum tri-isopropoxide (ATI) on a p-type germanium substrate in a CVD process. He achieved deposition rates of 67-100 Å/min. The ATI bubbler was kept at 125 °C and a flow rate of 1 L/min was used. The substrate temperature was 420 °C. Film thickness was typically 2000 Å. He found that the total flow rate does not affect deposition rate. The films made could be thermally cycled between 25 and 800 °C without developing crack lines, and the films were hard and transparent. Aluminum oxide films, along with silicon dioxide films, were exposed to 100% humidity at ambient temperature for 22 days. He found that the aluminum oxide films were more moisture resistant than the silicon dioxide films.

Temple (Ref 5) deposited aluminum oxide films on silicon substrates using aluminum hexafluoroacetate at temperatures of 350 to 450 °C by CVD. Film thicknesses, measured by 3-D wavelength ellipsometry, were 1500 to 2000 Å. Deposition rates were 10 to 60 Å/min. The films were amorphous and had smooth surfaces and good adherence. The chemical composition of the films was analyzed by x-ray photoelectron spectroscopy.

The films were carbon free when deposited in an oxygen atmosphere, but carbon was present when deposited in an argon atmosphere.
Saraie (Ref6, Ref7) used two different methods to deposit aluminum oxide films on silicon substrates. The first method was similar to Aboaf (Ref4), except that the decomposition reaction took place under reduced pressures and lower temperatures. Silicon substrates were used. The ATI bubbler was kept at 120 °C and all piping lines were kept at 130 °C. The total gas flow rate was 1 L/min, and flow through the bubbler was varied between 50 and 200 ml/min. The reactor pressure was 10 torr, and temperatures were between 250 and 450 °C. Plots of both temperature and flow rate versus deposition rate were prepared. These show that as both temperature and flow rate increase, the deposition rate increases. Also, an Arrhenius plot is shown that gives an activation energy of 18.2 Kcal/mole. Thickness uniformity was within 10%.

In the second method, aluminum oxide films were prepared by a two step electron beam evaporation process at temperatures as low as 250 °C. Films 1500 Å thick were made at a deposition rate of 240 Å/min with an oxygen pressure of 10⁻⁵ torr.

Mutoh (Ref8) made aluminum oxide films by CVD of ATI for use as a planar metallization technique to fabricate LSI chips. The bubbler temperature was kept at 170 °C, at which the vapor pressure of ATI is 50 mmHg. Deposition rates of 200 Å/min were obtained in a nitrogen atmosphere. Films were made up to 15000 Å thick. Thicker films developed cracks.
Mantese (Ref 9) has prepared aluminum oxide films by a process involving the reaction of aluminum oxide with water. Upon curing, a thin film is formed. This material is dispersed in droplet form and cured at 500 °C for 60 min. This low viscosity, clear liquid is placed on a substrate and spun at 3000 rpm for 30 seconds. To cure the soft phase material, the substrate is placed in an air oven, and the temperature is ramped at 15 °C per minute to a maximum of 500 °C and held there for 60 minutes. Films up to 1000 Å thick were made by this method.

Netterfield (Ref 10) used ion-assisted deposition to make 1000 Å thick aluminum oxide films. Aluminum was evaporated with simultaneous bombardment of the growing films with O₂⁺ ions. The films were characterized in situ by ellipsometry, multiwavelength transmittance photometry, and ion scattering spectroscopy.

2.3 Analysis of aluminum oxide films

Murphy (Ref 11) has determined elemental atomic percent profiles through the thickness of aluminum oxide films. He used X-ray Photoelectron Spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS), Secondary Ion Mass Spectroscopy (SIMS), and X-ray Diffraction (XRD). He found the elemental atomic percents at the surface to be aluminum (25%), oxygen (45%), and carbon (30%). At a depth of 1250 Å, the elemental atomic percents were aluminum (33%), oxygen (59%), and
carbon(8%). His data shows the carbon contamination at the surface is much greater than in the bulk of the film.
3.0 SAFETY AND HYGIENE

Aluminum tri-isopropoxide, CAS # 555-31-7, is a white, powdery solid that is harmless to the skin, but very dusty. When handling ATI, a dust mask, gloves, and safety glasses should be worn.

The main concern during the performance of the experiments is the possibility of burns by hot surfaces. High temperature gloves should be worn when handling the hot substrates.

When conducting the adhesion strength test the silicon substrate will shatter with force if it is placed improperly in the jaws. It is very important that safety glasses be worn at all times.
4.0 EXPERIMENTAL SETUP AND PROCEDURES

4.1 Experimental set-up

The deposition of aluminum oxide films on silicon and polyimide substrates was performed in a plasma enhanced chemical vapor deposition reactor. Aluminum Tri-isopropoxide (ATI) was heated in an oil bath to 120 °C. Argon was bubbled through the ATI.

The mixture of argon and ATI was metered through a rotameter. The reaction chamber was connected to the rotameter by 0.635 cm (1/4 inch) diameter stainless steel tubing wrapped with heat tape. The reaction chamber was evacuated by a mechanical pump. Within the reaction chamber, the substrate was heated by an electrical heater, and the temperature was measured by a thermocouple in contact with the surface of the heater.

The walls of the reaction chamber were cooled by passing water through copper coils brazed to the outside of the copper walls.

The reaction chamber was exposed to radio frequency waves of 13.56 MHz to create a plasma. The important process parameters are: substrate temperature, reaction chamber pressure, oil bath temperature, argon flow rate, RF power level, heat tape temperature, and oven temperature for weight
loss experiments. Figure 1 shows a schematic of the experimental setup.

The films produced were measured for thickness, thickness uniformity, adhesive strength, and weight loss of the polyimide composite.

The process of the reaction takes place in several steps. First, the ATI must diffuse from the bulk phase to the surface, where it is adsorbed. At the surface, a pyrolytic decomposition reaction occurs. The by-products of the reaction must then diffuse from the surface to the bulk phase.

The specifications of the equipment and chemicals used are as follows.

**Plasma reactor**: March Plasmod with a high temperature adapter designed by NASA Lewis Research Center.

**Flow meter**: Aalborg tube number 052-015T, 0-2000 ml/min.

**Oil bath**: Mineral oil in a beaker in a Glas-Col heating basket connected to a Glas-Col PL-312 Minitrol (1500 watts, 115 volts) rheostat. Temperature was measured by a 0-400 °C mercury thermometer.

**Substrate heater control**: Glas-Col PL-312 Minitrol (1500 watts, 115 volts) rheostat.

**Substrate temperature measurement**: Type J thermocouple connected to an Omega HHM57 digital multimeter.
Reaction chamber pressure measurement: Granville-Phillips 280 gauge controller connected to a Granville-phillips thermocouple gauge tube number 270006-1.

Vacuum pump: Alcatel 1004AC 1/2 hp mechanical oil seal medium vacuum pump, with a displacement of 3.2 cfm and capable of a vacuum of 0.05 mtorr.

Heat tape: Glas-Col 140 watt heat tape connected to a Glas-Col PL-312 Minitrol (1500 watt, 120 volts) rheostat.

Oven: Lindberg type 51894, 240 volts, 3500 watts.

Balance: Sartorius 1207MP2A with four decimal accuracy.

Thickness measurement: Sloan Dektak IIA.

Adhesion strength tester: Sebastian Five-A using Z module.

Aluminum tri-isopropox ide: Aldrich Chemicals 98+%, CAS # [555-31-7].


Silicon Wafers: Monsanto SN# 0026692.

Chemical composition analysis: Edward’s Accelerator Laboratory at Ohio University.

4.2 Procedures

General procedure for preparing an aluminum oxide film on a silicon or polyimide composite:

1. Clean silicon substrate with acetone and place it on the substrate heater.
2. Turn vacuum pump on to reaction chamber.
3. Heat oil bath to 120 °C.
4. Heat substrate to desired temperature.
5. Turn on heat tape to obtain 130 °C.
6. When chamber has been evacuated to 0.2 to 0.4 torr, introduce argon to the reaction chamber through the bypass valve for two minutes.
7. Close bypass valve and open valve to bubbler at desired flow rate.
8. Turn on RF generator, balance, and set to desired wattage.
9. Take readings on ATI bubbler temperature, chamber pressure and substrate temperature every 5 to 10 minutes.
10. After desired time has passed turn off RF generator and cut off the flow to the chamber.
11. Turn off substrate heater and oil bath heater.
12. After substrate temperature has fallen below 100 °C, turn off vacuum and expose chamber to atmosphere.
13. Let sample cool to ambient.

Procedure for measuring film thickness and uniformity:

1. Turn on Dektek IIA.
2. Place sample to be measured on platform.
3. Level platform.
4. Input program of specifications for test.
5. Press test button.
6. If necessary level graph along known points.
7. Read off thickness where step occurs.

**Procedure for measuring film adhesion strength:**

1. Turn on Sebastian Five-A adhesion tester and the attached computer.
2. Follow instructions provided to put the epoxy coated studs in place.
3. Heat oven to 150 °C.
4. Place samples with studs on ceramic plate and place in oven for one hour to cure.
5. Take out of oven and allow to cool to ambient temperature.
6. Remove stud holder.
7. Carefully place stud in jaws. Sample should be parallel to floor. The stud should be perpendicular to machine and set 0.25 inches out of the jaws.
8. Tighten jaws on stud.
9. Press start button and record data.

**Procedure for weight loss experiment:**

1. Weigh coated polyimide sample along with uncoated sample on a scale with ±0.0001 gram accuracy.
2. Heat oven to desired temperature.
3. Place coated and uncoated samples on ceramic plate and put inside oven.

4. Remove from oven at desired time interval and weigh.

**Procedure for chemical composition analysis of film:**

Films were analyzed at the Edward’s Accelerator Lab at Ohio University, using Rutherford Backscattering Spectroscopy (RBS).

**4.3 Experiments**

Experiments were designed to obtain data for the following:

- Deposition rate versus temperature
- Deposition rate versus flow rate
- Adhesion strength versus temperature
- Adhesion strength versus flow rate
- Adhesion strength versus thickness
- Adhesion strength versus deposition rate
- Thickness uniformity
- Reduction in weight loss of polyimide composite
- Chemical composition analysis
5.0 RESULTS AND DISCUSSION

One problem that occurred during the experiments that had an effect on the results was that the unheated rubber tubes inside the plasmod that connects the inlet tube to the reaction chamber would fill with condensed aluminum tri-isopropoxide. This greatly reduced the concentration of reactant in the reaction chamber.

5.1 Chemical composition analysis

Figure 2 shows an RBS plot of a film made from aluminum tri-isopropoxide. RBS was carried out at the Edward's Accelerator Lab at Ohio University, the spectrum was analyzed by the RUMP program. The results indicate a film of atomic ratio, $\text{Al}_1\text{O}_{1.6}\text{C}_{0.1}$. This shows an almost stoichiometric film of $\text{Al}_2\text{O}_3$ with 3.7% by weight elemental contamination of carbon.

RBS utilizes the elastic collisions between incident energetic ions and the nuclei of target atoms to measure the masses of the target atoms. Helium ions accelerated to 2.0 Mev were used as the incident ions. The ion beam is directed at the target through a series of magnets. By measuring the return energy and return angle, an atomic composition distribution of the target can be derived.
Figure 2. RBS Plot of Al2O3 Film

Energy (MeV)

Channel

Normalized Yield

carbon

oxygen

aluminum
In Figure 2 the arrows point to steps where the elemental masses of aluminum, carbon and oxygen reflect the incident ions.

5.2 Process parameters and data

Table 1 gives a summary of the process parameters studied and the resulting data. The reactor pressure was held constant at 0.8 ± 0.1 torr. The ATI bubbler temperature was held constant at 120 ± 2 ºC.

5.3 Temperature versus deposition rate

Figure 3 shows a plot of temperature versus deposition rate. These experiments were run at a constant flow (750 ml/min) of argon through the ATI bubbler. The plot indicates that as the substrate temperature is increased, the deposition rate increases. At temperatures of 250 and 400 ºC, deposition rates of 42.6 Å/min and 100.8 Å/min, respectively, were achieved. This means that the reaction is proceeding faster at higher temperatures, which is consistent with kinetic theory. These results are similar to those obtained by other researchers (Ref6,7), except that the deposition rates at the same temperatures are lower in our experiments. Also, the line has a smaller slope. This will be discussed in the next section.
FIGURE 3. DEPOSITION RATE VERSUS TEMPERATURE

AL2O3 FILM MADE AT 750ML/MIN
<table>
<thead>
<tr>
<th>SUBSTRATE TEMP C</th>
<th>FLOW RATE L/MIN</th>
<th>FILM THICK A</th>
<th>TIME MIN</th>
<th>DEP RATE A/MIN</th>
<th>PEEL STRENGTH N/M²</th>
<th>FILM UNIFORMITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>750</td>
<td>1275</td>
<td>30</td>
<td>42.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>750</td>
<td>1280</td>
<td>30</td>
<td>42.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>750</td>
<td>1472</td>
<td>30</td>
<td>49.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>275</td>
<td>750</td>
<td>1560</td>
<td>30</td>
<td>52.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>750</td>
<td>2184</td>
<td>30</td>
<td>72.8</td>
<td>60.86</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>750</td>
<td>2054</td>
<td>30</td>
<td>68.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>750</td>
<td>2545</td>
<td>30</td>
<td>84.8</td>
<td>69.4</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>750</td>
<td>2580</td>
<td>30</td>
<td>86.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>500</td>
<td>2430</td>
<td>30</td>
<td>81.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>500</td>
<td>2340</td>
<td>30</td>
<td>78.0</td>
<td>56.5</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>275</td>
<td>2050</td>
<td>30</td>
<td>68.3</td>
<td>37.35</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>275</td>
<td>2190</td>
<td>30</td>
<td>73.0</td>
<td>8.7</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>750</td>
<td>2965</td>
<td>30</td>
<td>98.8</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>375</td>
<td>750</td>
<td>2805</td>
<td>30</td>
<td>93.5</td>
<td>100.6</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>750</td>
<td>4500</td>
<td>45</td>
<td>100.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>750</td>
<td>3038</td>
<td>30</td>
<td>101.6</td>
<td>133.5</td>
<td></td>
</tr>
</tbody>
</table>
The deposition rate is calculated by dividing the thickness of the film by the deposition time.

5.4 Reaction activation energy - Arrhenius plot

Figure 4 shows an Arrhenius plot. To calculate activation energy, the equation used was:

\[ \ln \left( \text{Deposition Rate} \right) = \ln \left( A \right) - \frac{E}{RT} \]

where A is the Arrhenius constant
E is activation energy in Kcal/mole
R is the gas law constant
T is temperature in Kelvin

Thus, the slope of the Arrhenius plot is equal to \(-\frac{E}{RT}\). The activation energy of the reaction of aluminum tri-isopropoxide to aluminum oxide was found to be 4.2 Kcal/mole. Other researchers have found a value of 18.2 Kcal/mole (Ref6) using a simple CVD reactor. Even though the deposition rates found using the plasmod were lower at a given temperature, the activation energy was lower as indicated by the lower slope of the Arrhenius plot.

The lower slope is apparently due to the effect of the RF plasma. The decomposition reaction apparently proceeds by a different mechanism.
FIGURE 4. ARRHENIUS PLOT TO DETERMINE ACTIVATION ENERGY
5.5 Flow rate versus deposition rate

Figure 5 shows a plot of deposition rate versus flow rate of argon through the ATI bubbler at constant pressure. These experiments were run at a constant substrate temperature of 325 °C. The plot shows a trend of increasing deposition rate with increasing flow rate. Increasing the flow rate to the reaction chamber has the effect of increasing the concentration at the reaction surface. The steps to the reaction are diffusion to the surface from the bulk phase, adsorption to the surface, reaction at the surface, and diffusion from the surface of reaction by products. By increasing the flow rate in the bulk phase, the velocity of the bulk phase is increased. The increase of velocity has the effect of increasing the mass transfer coefficient, which increases the flux of ATI to the surface. The trend shown is consistent with the finding of other researchers.

5.6 Adhesion strength of Al₂O₃ films to silicon substrates

Films prepared as described above were tested for adhesion strength with a Sebastian V-A adhesion tester using the Z module. Figure 6 show a plot of adhesion strength versus substrate temperature. All films were made at a constant flow rate of 750 ml/min. The plot shows a definite trend of increasing adhesion strength with increasing temperature. This could be due to two factors: 1) deposition rate (film thickness) or, 2) the mechanism by which the reaction takes
FIGURE 5. DEPOSITION RATE VERSUS FLOW RATE

AL2O3 FILMS AT 325C
FIGURE 6. ADHESION STRENGTH OF AL2O3 FILMS ON SILICON SUBSTRATES

STRENGTH VS TEMPERATURE AT 750 ml/min

STRENGTH (N/M² x 10E6)

TEMPERATURE (C)
place at the surface of the substrate at each temperature. The film thickness increases with temperature at a given deposition time and flow rate.

Figure 7 shows a plot of adhesion strength versus flow rate of argon through the ATI bubbler. All films were made at a constant substrate temperature of 325 °C. The plot shows a trend of increasing adhesion strength with increasing flow rate. Again, this could be due to two factors: 1) film thickness or, 2) the mechanism by which the reaction takes place at the surface of the substrate at each flow rate. The film thickness increases with increasing flow rate.

Figure 8 shows a plot of adhesion strength versus deposition rate. The plot shows a general trend of increasing adhesion strength with increasing deposition rate. This is only single point data. The trend is not exact. The adhesion strength of a film made at a deposition rate of 68.5 Å/min has an adhesion strength of 4.7x10^6 N/M^2, where a film made at a deposition rate of 81 Å/min has an adhesion strength of 4.36x10^6 N/M^2.

With the data presently available, it is not understood exactly what the interaction between temperature and flow rate is to the effect on adhesion strength. A set of experiments will be outlined in the Recommendations section to separate the effects of temperature and flow rate on adhesion strength.
FIGURE 7. ADHESION STRENGTH OF Al2O3 FILMS ON SILICON SUBSTRATES
STRENGTH VS FLOW RATE AT 325°C

STRENGTH (N/m² x 10E6)

FLOW RATE (m/min)

2 2.5 3 3.5 4 4.5 5 5.5 6 6.5
200 250 300 350 400 450 500 550 600 650 700 750 800 850 900
FIGURE 8. ADHESION STRENGTH OF AL2O3 FILMS ON SILICON SUBSTRATES

STRENGTH VERSUS DEPOSITION RATE
5.7 Film thickness uniformity

Three films were tested for thickness uniformity. The calculation used to determine thickness uniformity was:

\[
\text{Variation} = 100 \frac{(D_{\text{max}} - D_{\text{min}})}{(D_{\text{min}} + D_{\text{max}})}
\]

where \( D \) is film thickness.

The measurements and results are given in Table 2.

Table 2. Film thickness uniformity measurements.

<table>
<thead>
<tr>
<th>Temperature(°C)</th>
<th>400</th>
<th>375</th>
<th>325</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate(ml/min)</td>
<td>750</td>
<td>750</td>
<td>275</td>
</tr>
<tr>
<td>Film thickness(Å)</td>
<td>4500</td>
<td>2965</td>
<td>2190</td>
</tr>
<tr>
<td></td>
<td>4625</td>
<td>2620 min</td>
<td>1875 min</td>
</tr>
<tr>
<td></td>
<td>4380 min</td>
<td>2950</td>
<td>2050</td>
</tr>
<tr>
<td></td>
<td>4725 max</td>
<td>2820</td>
<td>2234 max</td>
</tr>
<tr>
<td></td>
<td>4490</td>
<td>3010 max</td>
<td>2125</td>
</tr>
<tr>
<td>Variation(%)</td>
<td>3.8</td>
<td>6.9</td>
<td>8.7</td>
</tr>
</tbody>
</table>

All films measured exhibited a thickness variation of less than 10%, which is consistent with what has been reported in the literature. (Ref1,3,6,8)
5.8 Reduction in weight loss of polyimide composite

Two polyimide composite samples were coated with Al₂O₃ films of 1200 Å thickness at a substrate temperature of 325 °C and a flow rate of 500 ml/min. The deposition rate was 80 Å/min and the reaction took place for 15 minutes, yielding a thickness of 1200 Å. The coated polyimide samples, along with an uncoated polyimide control sample, were placed in an oven at 391 °C for 300 hours, and the mass of the sample was measure every 24 hours.

Figure 9 shows a plot of percent original mass versus time for each of the three samples. The plot shows a reduction in weight loss of the two coated samples over the uncoated sample.

It should be noted that, after 168 hours, the carbon fibers of the uncoated composite sample separated. After 216 hours one of the coated sample’s fibers started separating, and after 240 hours the other coated sample’s fibers separated. The samples’ fibers separated because enough of the PMR-15 had thermally oxidized to break the structure of the composite.
FIGURE 9. PERCENT ORIGINAL MASS
AL2O3 COATED POLYIMIDE AT 325 DEG C AND 500 mL/MIN

% ORIGINAL MASS

STANDARD
1200A AL2O3
1200A AL2O3

TIME (hours)
Figure 10 shows a plot of average percent improvement versus time for the coated samples over the uncoated sample. To obtain this data, the percent weight loss for the two samples were averaged. Percent improvement was calculated by the equation:

\[
\text{IMP} = \frac{\text{Percent Mass Loss Uncoated} - \text{Percent Mass Loss Coated}}{\text{Percent Mass Loss uncoated}}
\]

The percent improvement levels off at about 25% after 168 hours.

Figure 11 shows a plot of weight loss for several uncoated polyimide samples from different batches of polyimide as supplied by NASA. There is a large variation in weight loss from polyimide to polyimide, showing that the quality of polyimide we receive is not consistent. This problem is being discussed and addressed with NASA people who supply us the material.
FIGURE 10. AVERAGE PERCENT IMPROVEMENT IN WEIGHT LOSS
AL203 COATED POLYIMIDE
FIGURE 11. PERCENT ORIGINAL MASS UNCOATED POLYIMIDE COMPOSITES

- 390°C
- 371°C
- 317°C

100.0% ~ 50.0% ~ 30.0% ~ 20.0% ~ 10.0%

TIME (hours)
6.0 CONCLUSIONS

6.1 Preparation of aluminum oxide films

Several conclusions can be drawn from the data obtained from the experiments performed.

1. Aluminum oxide films can be prepared from aluminum tri-isopropoxide using plasma enhanced chemical vapor deposition in near stoichiometric amounts with little carbon contamination. They can be made on silicon and polyimide composite substrates, over a temperature range of 250 to 400 °C, and over an argon flow rate through the ATI bubbler of 275 to 750 ml/min.

2. The data indicate that as substrate temperature increases deposition rate increases.

3. The data indicate that as argon flow through the ATI bubbler increases deposition rate increases.

4. The effect of the RF plasma is to reduce the activation energy required by heat, thus reducing the temperature at which a given rate of reaction takes place.

5. The adhesion strength of the aluminum oxide films on a silicon substrate increases as the temperature of the reaction increases.

6. The adhesion strength of aluminum oxide films on a silicon substrate increases as the flow rate of argon through the ATI bubbler increases.
7. There is not enough data at present to know how temperature and flow rate together affects the adhesion strength.

6.2 Coating of polyimide composites with Al₂O₃ films

1. Coating of a polyimide composite with a thin film of Al₂O₃ is effective in increasing the thermo-oxidative stability of the polyimide composite by 25% over a period of 300 hours. The film apparently accomplishes this by acting as a barrier to oxygen.

2. The quality of the polyimide composite received from NASA is variable.
7.0 Recommendations

1. Design a set of experiments to get a better understanding of the interactive effects of temperature and flow rate on adhesion strength. These experiments should include:

   A. Strength versus temperature at constant film thickness and flow rate.
   B. Strength versus flow rate at constant film thickness and temperature.
   C. Strength versus film thickness at constant temperature and flow rate.

2. A series of experiments should be done to study the effect of adhesion strength of Al₂O₃ films on polyimide composite mass loss at elevated temperatures with a constant film thickness.

3. A series of experiments should be done to study the effect of Al₂O₃ film thickness on polyimide composite mass loss at elevated temperatures.

4. A set of experiments should be performed to study the effect of the RF plasma on both the adhesion strength of the Al₂O₃ films and the mass loss of polyimide composites. A series of studies should be done in the PECVD reactor and a conventional(thermal) CVD reactor under the same conditions and the results compared.
5. Consult with NASA to obtain a consistent quality of polyimide composite.

6. Consult with the manufacturer of the Plasmod to solve the problem of condensation in the tubes of the inlet to the reaction chamber.
8.0 REFERENCES


