INFORMATION TO USERS

This reproduction was made from a copy of a document sent to us for microfilming. While the most advanced technology has been used to photograph and reproduce this document, the quality of the reproduction is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help clarify markings or notations which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure complete continuity.

2. When an image on the film is obliterated with a round black mark, it is an indication of either blurred copy because of movement during exposure, duplicate copy, or copyrighted materials that should not have been filmed. For blurred pages, a good image of the page can be found in the adjacent frame. If copyrighted materials were deleted, a target note will appear listing the pages in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed, a definite method of "sectioning" the material has been followed. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For illustrations that cannot be satisfactorily reproduced by xerographic means, photographic prints can be purchased at additional cost and inserted into your xerographic copy. These prints are available upon request from the Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases the best available copy has been filmed.
High frequency dielectric properties of polyimides for multilayer interconnect structures

Hinedi, Mohamad Fahd, M.S.

The University of Arizona, 1987
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark √.

1. Glossy photographs or pages ✓
2. Colored illustrations, paper or print □
3. Photographs with dark background ✓
4. Illustrations are poor copy □
5. Pages with black marks, not original copy ✓
6. Print shows through as there is text on both sides of page □
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements □
9. Tightly bound copy with print lost in spine □
10. Computer printout pages with indistinct print □
11. Page(s) ______ lacking when material received, and not available from school or author.
12. Page(s) 27 seem to be missing in numbering only as text follows.
13. Two pages numbered □. Text follows.
14. Curling and wrinkled pages □
15. Dissertation contains pages with print at a slant, filmed as received ✓
16. Other ________________________________________________________________

_____________________________________________________________________

_____________________________________________________________________

University
Microfilms
International
HIGH FREQUENCY DIELECTRIC PROPERTIES
OF
POLYIMIDES FOR MULTILAYER INTERCONNECT STRUCTURES

by

Mohamad Fahd Hinedi

A Thesis Submitted to the Faculty of the
DEPARTMENT OF ELECTRICAL AND COMPUTER ENGINEERING
In Partial Fulfillment of the Requirements
For the Degree of
MASTER OF SCIENCE
WITH A MAJOR IN ELECTRICAL ENGINEERING

In the Graduate College
THE UNIVERSITY OF ARIZONA

1987
STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: [Signature]

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

[Signature] Barry C. Johnson
Professor of Electrical and Computer Engineering

6/19/87 Date
This thesis is dedicated to my parents

Laila and Jamil.

Special thanks for their support and encouragement.
ACKNOWLEDGMENT

I would like to express my sincere appreciation to Dr. Barry Johnson for the careful guidance, generous time, and constructive criticism he gave throughout this study.

My deep appreciation and thanks to Dr. Ronald Schrimpf and Dr. Olgierd A. Palusinski for their helpful suggestions and for serving as members of the examining committee.

I give special thanks to fellow graduate student Hamid Rasafar for his helpful suggestions.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Illustrations</td>
<td>vii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>ix</td>
</tr>
<tr>
<td>Abstract</td>
<td>x</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Why the Concern over Dielectric Constant and Loss Tangent?</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Why Polyimide?</td>
<td>7</td>
</tr>
<tr>
<td>1.2.1 Design Guidelines for High Performance Packaging</td>
<td>7</td>
</tr>
<tr>
<td>1.2.2.1 Chemistry of Polyimides</td>
<td>9</td>
</tr>
<tr>
<td>1.2.2.2 The Imidization Reaction</td>
<td>9</td>
</tr>
<tr>
<td>1.3 Purpose</td>
<td>10</td>
</tr>
<tr>
<td>2. Experimental Procedure</td>
<td>11</td>
</tr>
<tr>
<td>2.1 Sample Preparation</td>
<td>11</td>
</tr>
<tr>
<td>2.1.1 Spin-On Method</td>
<td>11</td>
</tr>
<tr>
<td>2.1.2 Sheet Method</td>
<td>16</td>
</tr>
<tr>
<td>2.2 Measurement Techniques</td>
<td>16</td>
</tr>
<tr>
<td>2.2.1 Low Frequency Method: ASTM</td>
<td>16</td>
</tr>
<tr>
<td>2.2.2 High Frequency Method</td>
<td>21</td>
</tr>
<tr>
<td>2.3 Characterization Methods</td>
<td>23</td>
</tr>
<tr>
<td>2.3.1 RBS Analysis</td>
<td>26</td>
</tr>
<tr>
<td>2.3.2 Talysurf Measurements</td>
<td>26</td>
</tr>
<tr>
<td>2.3.3 Alphastep Measurements</td>
<td>26</td>
</tr>
<tr>
<td>3. Experimental Results</td>
<td>28</td>
</tr>
<tr>
<td>3.1 Frequency Dependence</td>
<td>28</td>
</tr>
<tr>
<td>3.1.1 Low Frequency Dependence</td>
<td>28</td>
</tr>
<tr>
<td>3.1.2 High Frequency Dependence</td>
<td>32</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS--Continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2 Cure Time Dependence</td>
<td>43</td>
</tr>
<tr>
<td>3.3 Thickness Dependence</td>
<td>45</td>
</tr>
<tr>
<td>3.4 Temperature Dependence</td>
<td>47</td>
</tr>
<tr>
<td>3.5 Electrode Composition and Thickness Analysis</td>
<td>48</td>
</tr>
<tr>
<td>4. Discussion</td>
<td>52</td>
</tr>
<tr>
<td>4.0 General Dielectric Properties</td>
<td>52</td>
</tr>
<tr>
<td>4.1 Frequency Dependence</td>
<td>55</td>
</tr>
<tr>
<td>4.1.1 Low Frequency Dependence</td>
<td>55</td>
</tr>
<tr>
<td>4.1.2 High Frequency Dependence</td>
<td>56</td>
</tr>
<tr>
<td>4.2 Temperature Dependence</td>
<td>59</td>
</tr>
<tr>
<td>4.3 Thickness Dependence</td>
<td>59</td>
</tr>
<tr>
<td>4.4 Cure-Time Dependence</td>
<td>60</td>
</tr>
<tr>
<td>4.5 Compatibility with Multilayer Interconnect Structures</td>
<td>61</td>
</tr>
<tr>
<td>5. Conclusion</td>
<td>63</td>
</tr>
<tr>
<td>References</td>
<td>65</td>
</tr>
<tr>
<td>Selected Bibliography</td>
<td>66</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1 Basic Interconnect Geometries: (a) One Signal Plane Microstrip; and (b) One Signal Plane Stripline</td>
<td>4</td>
</tr>
<tr>
<td>Figure 1.2 Coated or Embedded Microstrips: (a) Coated Microstrip; (b) Embedded Microstrip; (c) Pair of Signal Planes Microstrip, and (d) Pair of Signal Planes - Stripline</td>
<td>5</td>
</tr>
<tr>
<td>Figure 1.3 Propagation Delay versus Dielectric Constant</td>
<td>6</td>
</tr>
<tr>
<td>Figure 2.1 Spin Speed of Probimide 293 versus Film Thickness</td>
<td>12</td>
</tr>
<tr>
<td>Figure 2.2 Steps for Structuring Ciba-Geigy's Polyimide Coatings</td>
<td>15</td>
</tr>
<tr>
<td>Figure 2.3 ASTM's Structure for Unequal Electrodes</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2.4 Top View of the Spin-on Capacitor Structures</td>
<td>19</td>
</tr>
<tr>
<td>Figure 2.5 HP4192A LF Impedance Analyzer</td>
<td>20</td>
</tr>
<tr>
<td>Figure 2.6 HP16047C Test Fixture</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2.7 Error Reading versus Frequency for LF Impedance Analyzer</td>
<td>22</td>
</tr>
<tr>
<td>Figure 2.8 HP4191A RF Impedance Analyzer</td>
<td>24</td>
</tr>
<tr>
<td>Figure 2.9 HP16091A Coaxial Fixture Set</td>
<td>25</td>
</tr>
<tr>
<td>Figure 3.1 Dielectric Constant of Probimide 293 versus Frequency</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.2 Dissipation Factor of Probimide 293 versus Frequency</td>
<td>31</td>
</tr>
<tr>
<td>Figure 3.3 Dielectric Constant of Probimide 293 (Ag Electrodes) versus Frequency</td>
<td>33</td>
</tr>
</tbody>
</table>

vii
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 3.4</td>
<td>Dissipation Factor of Probimide 293 (Ag Electrodes) versus Frequency</td>
<td>35</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Dielectric Constant of Probimide 293 (Al Electrodes) versus Frequency</td>
<td>36</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Dissipation Factor of Probimide 293 (Al Electrodes) versus Frequency</td>
<td>37</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Dielectric Constant of PI2555 versus Frequency</td>
<td>38</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Dissipation Factor of PI2555 versus Frequency</td>
<td>40</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Dielectric Constant of PI2545 versus Frequency</td>
<td>41</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>Dissipation Factor of PI2545 versus Frequency</td>
<td>42</td>
</tr>
<tr>
<td>Figure 3.11</td>
<td>Dielectric Constant of Probimide 293 versus Frequency</td>
<td>44</td>
</tr>
<tr>
<td>Figure 3.12</td>
<td>Dissipation Factor of Probimide 293 Frequency</td>
<td>46</td>
</tr>
<tr>
<td>Figure 3.13</td>
<td>Dielectric Constant of Probimide 293 versus Temperature</td>
<td>48</td>
</tr>
<tr>
<td>Figure 3.14</td>
<td>RBS plot of Aluminum on Carbon</td>
<td>49</td>
</tr>
<tr>
<td>Figure 3.15</td>
<td>(Blow Up) of RBS Plot of Aluminum on Carbon</td>
<td>50</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Schematic Diagram of Variation of Dielectric Properties for a Material</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>Having Electronic, Atomic, Orientation and Space Charge Polarizations (8)</td>
<td></td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Typical Package for Multilayer Interconnection Structure</td>
<td>62</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table                                      Page

3.1 Sample Specification for Low Frequency Measurements .............................. 29

3.2 Sample Specification for High Frequency Measurements ............................ 32

3.3 Sample Specification for Cure-Time Dependence ................................. 43

3.4 Dielectric Constant Variation with Thickness ......................................... 45
ABSTRACT

One of the most important electrical requirements in high performance electronic systems or high speed integrated circuits, is to process larger numbers of electrical signals at much higher speeds. Signal propagation delay must be minimized in order to maximize signal velocities. Therefore, material with low dielectric constant and low dissipation factor is being sought. In this thesis research measurements of dielectric constant and dissipation factor were performed on commercially available polyimides that are used in multilayer interconnect structures. Capacitor structures with a polyimide dielectric were measured up to a 1GHz frequency and 220°C temperature. Polyimides were concluded to be compatible for use in high performance systems such as multilayer interconnect structures.
CHAPTER 1

INTRODUCTION

The need to minimize off-chip signal propagation delay is essential in order to process signals in electronic systems at much higher speeds. Therefore, substrate (packaging) materials with low dielectric constant $\varepsilon_r$ and a low dissipation factor $D$ are being sought. Polyimide has been recently shown to be a promising candidate to meet all electrical property requirements from room temperature to $500^\circ C$.

The dielectric properties of polyimide materials above 1MHz in frequency and $25^\circ C$ in temperature have not been reported. Because such data is of great importance to microelectronic and electronic applications, it is the intent of this thesis research to measure the dielectric constant and dissipation factor of commercially available polyimides as a function of deposition conditions, measurement conditions, frequency and temperature.

1.1 Why the Concern over Dielectric Constant ($\varepsilon_r$) and Loss Tangent (D)

Electrically, interconnect lines between integrated circuits are characterized by the wave length of the signal propagating through them and by their length. Interconnect line lengths, at the printed circuit board level, can vary
from less than an inch up to three feet. When low frequencies (long wave lengths) are propagated, their approximate equivalent circuit is resistive, but when high frequencies (short wave lengths) are propagating through interconnect lines, their equivalent circuit becomes a distributed transmission line network. An illustration follows showing when to treat an interconnect line as a resistive, lumped or distributed transmission line network (1,2).

\[
\begin{align*}
1 &< \lambda/10,000 & \text{Resistive} \\
\lambda/10,000 &< 1 < \lambda/20 & \text{Lumped} \\
\lambda/20 &< 1 & \text{Distributed} \quad (1.1)
\end{align*}
\]

where

\[
\begin{align*}
l & = \text{length of interconnect line} \\
\lambda & = \text{wave length of propagation signal in feet} \\
\lambda & = 2.81 \times \frac{t_r}{\sqrt{\varepsilon_r}} \\
t_r & = \text{rise time of propagation signal in nsec} \\
\varepsilon_r & = \text{the effective dielectric constant of the material}
\end{align*}
\]

The need for higher speeds—that is, shorter times—is also causing printed circuit board vias and connectors to behave as distributed transmission lines. Ideally the desired lines and connectors should have zero lengths; this will make the delay zero. No such ideal lines or connectors exist in practice, since finite line lengths as well as connectors are required. Well designed short lengths of lines, and matching terminations and connectors are
essential to keep generated reflection noise, cross talk noise, and signal attenuation to an acceptable level (1,2).

There are two basic interconnection transmission line geometries used in integrated circuit packaging, the microstrip and the stripline, as shown in Figure 1.1. Both microstrip and stripline can be batch fabricated in the form of printed circuit boards and thick or thin film hybrid circuits. Variations of these geometries are shown in Figure 1.2. They include the coated microstrip, embedded microstrip, pair of signal planes—microstrip and pair of signal planes—stripline. Signal propagation delay and, conversely, signal velocity along a microstrip or stripline (or variation thereof) are square root functions of the material dielectric constant

\[ t_d \propto \sqrt{\varepsilon_r} \]  

(1.2)

where

- \( t_d \) = propagation delay
- \( \varepsilon_r \) = effective dielectric constant of the material.

Therefore, greater control over \( \varepsilon_r \) will result in greater control of propagation delay. In high speed systems, the dielectric constant \( \varepsilon_r \) being sought is about 4.0 or below. A graph of propagation delay time versus dielectric constant is shown in Figure 1.3. Temperature variation can induce chemical changes and/or mechanical stresses in different materials that can cause the dielectric constant to vary. Moreover, frequency variation will also cause the
Figure 1.1 Basic Interconnect Geometries: (a) One Signal Plane Microstrip; and (b) One signal plane Stripline.
Figure 1.2 Coated or Embedded Microstrips: (a) Coated Microstrip; (b) Embedded Microstrip; (c) Pair of Signal Planes - Microstrip and; (d) Pair of Signal planes - Stripline.
Figure 1.3 Propagation Delay versus Dielectric Constant.
dielectric constant to vary. Hence, the behavior of dielectric constant with temperature and frequency should be well understood before use in electronic system designs.

Clearly, with current high speeds and shorter rise times, the problem of transporting pulses with maximum fidelity has become a serious one. Minimum attenuation and dispersion in the transport process are required. For this purpose, material with small loss tangent ($\tan\delta$) as well as low dielectric constant is required.

1.2 Why Polyimide

1.2.1 Design Guidelines for High Performance Packaging

In general, high performance systems requiring high interconnect densities are currently being designed using the following guidelines (3):

1. Spacing integrated circuits as closely as the cooling technique allows, in order to minimize interconnect line lengths.

2. Interconnecting integrated circuits through high aspect ratio (large thickness/width) signal lines of high conductivity material, in order to achieve high wiring densities.

3. Separating signal lines from ground planes with a relatively thick layer of a low dielectric material.

4. Separate conductor lines as far as signal wiring layers allow.

We can execute the above guidelines accurately if we can find a material with a low dielectric constant and low loss tangent ($\tan\delta$), and at the same time it can withstand
temperatures generated by the fabrication process. Moreover, it must perform reliably during use in a high performance system or package.

Polyimide is an advantageous dielectric for many reasons. As a class, polyimide polymers possess outstanding combinations of properties and retain those properties from room temperature up to 500°C for a considerable period of time. The polymer is a viscous liquid that can be applied at desired thickness of 0.1-50 µm (0.003-2.0 mils) by spinning, spraying, or casting, providing partial planarization of conductor lines and accurate thickness control. Fully cured polyimide is mechanically tough and flexible and can withstand fabrication processes such as metal deposition, photolithography, wet etching and soldering. Polyimide can be patterned with high resolution by plasma etching. Moreover, and most importantly, polyimide has been reported to have a low dielectric constant between 2.0 and 4.0 at 1kHz and 25°C. Polyimide also has a high breakdown voltage (4). However, the values of dielectric constant and loss tangent in the frequency range (1MHz - 1GHz) and temperature range (25-200°C) of interest to high performance circuit and system designers have not, as yet, been reported.
1.2.2.1 Chemistry of Polyimides

Polyimides are copolymers made by condensation polymerization of an acid dianhydride and a diamino base. If condensations are carried out at room temperature or less, the polymerization stops with the formation of the polyamic acid (Compound I). The polyimide (Compound II) is obtained from thermal polymerizations or can be obtained from the polyamic acid in film form by heating to temperatures in excess of 200°C. The R' and R" groups can be aliphatic or aromatic, as shown:

\[
\begin{align*}
\text{acid dianhydride} & : R' - \overset{\text{O}}{\mid} - C - \overset{\text{O}}{\mid} - C - \overset{\text{O}}{\mid} - N - C - \overset{\text{O}}{\mid} - C - \overset{\text{O}}{\mid} - R" \\
\text{diamino base} & : \text{H}_n - \overset{\text{N}}{\mid} - C - \overset{\text{N}}{\mid} - R" \\
\text{polyamic acid} & : \text{I} \\
\text{polyimide} & : \text{II}
\end{align*}
\]

\[
\begin{align*}
\text{I} \xrightarrow{T=200^\circ\text{C}} \text{II} & \quad +2n\text{H}_2\text{O}
\end{align*}
\]

1.2.2.2 The Imidization Reaction

Most semiconductor process effort has been expended on the polyamic-acid-type resins, and it is important to understand the imidization reaction. Resins which have their
solvent removed at a low temperature and are converted to a different chemical form when cured at high temperatures are said to be "b stage" cured after the solvent is removed. A high temperature cure preceded by a b stage cure is known as an anneal. 1-methylpyrrolidinone (NMP), which is a solvent in most polyamic acids, has a boiling point of \(205^\circ\text{C}\). It's high vapor pressure at 100-120\(^{\circ}\text{C}\) allows thin polyamic acid films to be b staged after 30 minutes at these temperatures, with 80-85 percent of the NMP and other hydrocarbons (i.e., aromatic) that are present in the solvent to evaporate. Large onset of solvent loss starts at 120\(^{\circ}\text{C}\) and is only complete at the boiling point of NMP. Imidization is initiated at temperatures as low as 120\(^{\circ}\text{C}\). and not really complete until 200\(^{\circ}\text{C}\) or more (1,4).

1.3 Purpose

The purpose of this thesis is to apply modifications of the American Standard Test Methods (ASTM) and other techniques in order to study the dielectric constant and loss tangent \((\tan\delta)\) of polyimide in the frequency and temperature ranges 10Hz - 1GHz and 25-210\(^{\circ}\text{C}\), respectively. Polymides that have been used in this research are commercially available, widely used polymides for multilayer interconnect structures, i.e., Probimide 293 polyimide that has been furnished by Ciba-Geigy Corporation, and PI2545 and PI2555 polyimides that have been furnished by DuPont.
CHAPTER 2

EXPERIMENTAL PROCEDURE

The polyimides selected for investigation are Probimide 293, developed by Ciba-Giegy Corporation, and PI2545 and PI2555 that were developed by DuPont. These polyimides are used in many microelectronic applications and have numerous advantageous features including:

a) Excellent adhesion
b) No high temperature cure
c) High thermal stability
d) Easy method of application
e) Probimide 293 is supplied fully imidized, where no refrigeration is required and no volatiles are released during processing

2.1 Sample Preparation

The objective is to fabricate capacitor structures with polyimide as the dielectric material. In order to study the effect of film thickness and fabrication, two sample preparation procedures were used: the spin-on and the sheet procedures.

2.1.1 Spin-on Method

A layer of silicon dioxide is first deposited on a silicon wafer. Polyimide of thickness \( h \) is sandwiched
between two layers of vacuum deposited aluminum conductor electrodes of thickness \(a\), such that \(a \ll h\), in order to satisfy the ASTM specifications that are discussed in Section 2.2 of this chapter.

Details of the process steps used in fabricating the spin-on samples are summarized as follows:

A  **Wafer Cleaning:** Fifty p-type silicon wafers (2 inches in diameter, 12 ± 1 mil thick, 0.01 - 0.022\(\Omega\)cm resistivity and <111> orientation) were used as substrates. The wafers were cleaned according to the following procedure:

1. **Ultrasonic Solvent:** Submerge the wafers in a beaker full of acetone and put beaker in an ultrasonic cleaner for 10 minutes.
2. **Rinse:** Rinse wafers in deionized (DI) water for 5 minutes.
3. **Acid Soak:** Submerge the wafers in a boat containing a solution of Piranha (6:1 \(H_2SO_4:H_2O_2\)) at a temperature of 85-90°C for 10 minutes.
4. **Rinse:** Rinse wafers in DI water for 5 minutes.
5. **Deglaze:** Dip wafers in a solution of buffered Hydrofloric Acid (10:1 \(H_2O:HF\)) until wafers are hydrophobic.
6. **Rinse:** Rinse wafers in DI water for 5 minutes and blow dry with Nitrogen gas.

B  **Oxide Growth:** A layer of silicon dioxide of thickness 10,000 \(\AA\) was grown on the surface of all wafers at 1160°C in steam. The layer of
Figure 2.1 Spin Speed of Probimide 293 versus Film Thickness.
SiO₂ was deposited in order to insulate any effects of the p-type silicon substrate from capacitance measurement.

C  Ground Plane Metalization: A layer of MOS quality Aluminum was vacuum deposited at 5x10⁻⁶ torr pressure onto the silicon dioxide layer of all wafers in a resistance-heated souke evaporator.

D  Application of Probimide 293 Polyimide:
  1. Wafer Preparation
     a) Dehydrate or bake wafers at 300°C for 30 minutes
     b) Apply diluted adhesion promoter. Dilute one part of QZ3289 concentrate with 9 parts of QZ3290 diluent. Both QZ3289 and QZ3290 are manufactured by Ciba-Geigy.
     c) Spin on at 5000 rpm for 20 seconds.
     d) Bake at 50°C for 2 minutes.
  2. Deposition of Polyimide
     a) Spin on desired thickness of polyimide per Figure 2.1 (3), which displays spin speed vs. film thickness for Probimide 293.
     b) Bake wafer using a hot plate at 85°C for 30 minutes, 150°C for 15 minutes, and 240°C for 15 minutes.
  3. Photoresist Mask Preparation
     a) Apply a one micron thick layer of KTI positive photoresist 1350-SF by spinning at 3500 rpm for 20 seconds.
     b) Soft bake at 90°C for 20 minutes.
     c) Expose wafer (120 nj at 405 nm).
d) Develop using (3.5:1 351KTI:DI water).

e) Rinse with DI water and blow dry with Nitrogen gas.

f) Hard bake patterned resists at 185°C for 120 minutes.

4. Polyimide Etch: Etching is required in order to open a window for contact to the ground plane metalization.

a) Immerse hard-baked, patterned wafer in QZ3296 etcher at 22°C for 90 seconds/micron of coating in an ultrasonic agitation. Last 10 seconds of etching should be done in clean etcher solution.

b) Rinse 30 seconds in DI water.

5. Photoresist Strip

a) Immerse wafer in QZ3298 at 47-50°C for 20 minutes maintaining slow, steady agitation.

b) Immerse wafer in a QZ3298 bath at room temperature maintaining slow agitation for 1 minute.

c) Rinse in DI water for 30 seconds.

Figure 2.2.(3) illustrates the steps of polyimide etching discussed above. Note that samples with polyimide thicker than 10 microns were deposited in layers. A cure cycle at 80°C for 30 minutes was performed after each deposited layer.

E. Top Metalization: A metal mask with a 1 inch diameter hole was placed on each wafer, and a layer of MOS quality aluminum was vacuum deposited at 5x10^-6 torr pressure onto the polyimide in a resistance-heated source evaporator.
1. Apply desired thickness of polyimide. Remove solvent.

2. Apply positive photoresist. Soft bake.

3. Expose and develop photoresist normally.

4. Hard bake patterned photoresist at 185° for 2 hours.

5. Etch polyimide in QZ 3296, 90 sec/micron of thickness.

6. Strip photoresist in QZ 3298 for 20 minutes at 47-50°C.

Figure 2.2 Steps for Structuring Ciba-Geigy's Polyimide Coatings.
2.1.2 Sheet Method

Sheets of fully cured and developed polyimides were received from both Ciba-Geigy and DuPont Corporations. A sheet of Probimide 293 (1 mil thick), two sheets of PI2555 (0.8 and 1.7 mils thick), and two sheets of PI2545 (1.0 and 1.7 mils thick) were metalized on both sides using two types of contact electrodes.

A. Aluminum Electrodes: MOS quality Aluminum was deposited on both sides of segments from all sheets using the same metalization procedure discussed in Section 2.1.1. Samples 10mm in diameter were cut for testing.

B. Silver Paste Electrodes: A layer of silver conductive paste was painted on both sides of all sheets. Samples of 10mm in diameter were cut for testing.

2.2 Measurement Techniques

Low frequency measurements (<10MHz) and high frequency measurements (>10MHz) were performed.

2.2.1 Low Frequency Method - ASTM

American standard test method (ASTM) for a-c loss characteristics and dielectric constant of solid electrical insulating materials were followed for the spin-on polyimide samples. These guidelines are suggested for measurements
done at frequencies between 1 Hz to a few MHz. According to the ASTM's general measurement considerations, when performing capacitance measurements, the effect of the fringing or edge capacitance $C_e$ should be subtracted from the measured value of the capacitance of the sample under test. For the case of unequal electrodes, as shown in Fig. 2.3, the edge capacitance is given by (5):

$$C_e = (0.0041kx - 0.003341nh + 0.0122)P$$  \hspace{1cm} (1)

where

- $C_e$ = fringing or edge capacitance in pF
- $P$ = perimeter of conductors in mm
- $kx$ = permittivity of the material
- $h$ = thickness of dielectric material in mm

hence

$$C_{\text{actual}} = C_{\text{measured}} - C_e$$

Figure 2.3 Unequal electrodes.
The upper Aluminum electrode comprises a ring of diameter equal to one inch. A top picture of the capacitor structure is shown in Fig. 2.4.

The equation for capacitance is then given by:

$$C = \varepsilon_o \varepsilon_r \frac{A}{h}$$

(2)

where

- $C$ = Capacitance = $C_{\text{measured}} - C_e$
- $\varepsilon_o$ = Permitivity of free space = $8.854 \times 10^{-12}$ F/m
- $\varepsilon_r$ = Dielectric constant of material
- $A$ = Area of capacitor
- $h$ = Thickness of dielectric material

Using the above equation to solve for dielectric constant, we get:

$$\varepsilon_r = \frac{(C_{\text{m}} - C_e) h}{C \varepsilon_o}$$

(3)

Inserting the appropriate values for $A$ and $h$ into Eq. 3 yields

$$\varepsilon_r = \frac{C h}{4.484 \times 10^{-15}}$$

(4)

An HP 4192A low frequency impedance analyzer (Fig. 2.5) was used to measure capacitance and dissipation factor for frequencies between 5Hz to 13MHz.

The low frequency impedance analyzer is a fully automatic, high performance test instrument designed for high precision measurements of impedance parameters. Measurement range of $C$ and $D$ are 0.1pF to 100.0 mF and 0.0001 to
Figure 2.4 Top View of Spin-On Capacitor Structures.
Figure 2.5 HP 4192A LF Impedance Analyzer.
19.999, respectively, with a basic accuracy of 0.1% and a resolution of 4 1/2 display digits. The 4192A has the capability to compensate for residuals present in the test fixture, test leads, and measurement circuit by using zero offset keys.

Test fixture HP 16047C (Fig. 2.6) was used in conjunction with the impedance analyzer to perform the measurements. Parameter reading errors vary from 0.01% at 1MHz to 1.8% at 13MHz and offset values in D vary from 0.0001 at 1MHz to 0.02 at 13MHz. A curve for parameter reading error and offset value in D vs. frequency is shown in Fig. 2.7.

2.2.2 High Frequency Method

For measurements at frequencies greater than 1MHz a different technique was employed. Samples were obtained from the sheet method discussed in Section 2.1.2 were cut in circles of 7.9mm (5/16 inches) in diameter. Dielectric constant was calculated using the following equation:

\[
\varepsilon_r = \frac{C_m h}{A \varepsilon_0}
\]

(5)

where: \(C_m\) = measured capacitance

Inserting the appropriate values of \(A\) and \(\varepsilon_0\) into Eq. 5 yields

\[
\varepsilon_r = \frac{C_m h}{4.379 \times 10^{-16}}
\]

(6)
Figure 2.6 HP 16047C Test Fixture.

Parameter reading error vs frequency. Offset value in D vs frequency.

Figure 2.7 Error Reading versus Frequency for LF Impedance Analyzer.
An HP 4191A radio frequency impedance analyzer (Fig. 2.8) was used to measure capacitance and dissipation factor for frequencies between 1-1000MHz.

The radio frequency impedance analyzer is a fully automatic, high performance test instrument designed for high precision measurements of impedance parameters of electronic devices and materials. The measurement ranges of C and D are 0.1pF to 1 \( \mu \)F and 0.0001 to 1000, respectively, with an accuracy of 1% and a resolution of 4 1/2 display digits. The 4191A must be calibrated at either the desired frequency range or the entire frequency range before taking any measurements. The calibration is performed under automatic settings of both the test parameter and frequencies using three kinds of reference terminations.

Test fixture HP 16091A coaxial resonant cavity (Fig. 2.9), was used in conjunction with the impedance analyzer to perform all high frequency measurements. The coaxial fixture has a frequency range of 1-1000 MHz.

2.3 Characterization Methods:

Rutherford Backscattering (RBS) analysis, talysurf measurements, and alphastep measurements were used to characterize the samples.
Figure 2.8 HP 4191A RF Impedance Analyzer.
Figure 2.9 HP 16091A Coaxial Fixture Set.
2.3.1 **RBS Analysis**

RBS analysis was performed with a 6MV Van DeGraaff at the Physics Department of the University of Arizona, in order to (1) measure the Aluminum electrode thickness, and (2) determine the identity and amount of any impurities introduced by the metalization process. Aluminum sample films were deposited onto a carbon substrate at the same time as the Aluminum electrodes were deposited onto the dielectric test samples.

2.3.2 **Talysurf Measurements**

Talysurf measurements were performed on the spin-on samples in order to measure polyimide thickness. Talysurf measurements were done at Burr-Brown Corporation in Tucson, Arizona.

2.3.3 **Alphastep Measurement**

Thickness measurements were also performed by an alphastep, which is available at the micro-electronics laboratory at the University of Arizona.

Thicknesses of both talysurf and alphastep techniques matched to within 8%.
Results of the measurements of dielectric constant and dissipation factor as a function of frequency, cure time, dielectric thickness, and temperature are given in this chapter.

3.1 Frequency Dependence

As mentioned in Chapter 2, frequency measurements were divided into two groups: low frequency and high frequency measurements. The results are therefore presented accordingly.

3.1.1 Low Frequency Dependence

Low frequency measurements in the range 10Hz to 1MHz were performed on samples fabricated using the spin-on method. Four major samples of different thicknesses were fabricated following the sample preparation guidelines given in Chapter 2 for the Probimide 293 polyimide. Table 3.1 illustrates the sample specifications.
TABLE 3.1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target Thickness</th>
<th>Measured Thickness</th>
<th>Number of Layers</th>
<th>Cure Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10 μm</td>
<td>10 μm</td>
<td>1</td>
<td>Standard*</td>
</tr>
<tr>
<td>B</td>
<td>10 μm</td>
<td>10 μm</td>
<td>2</td>
<td>Standard</td>
</tr>
<tr>
<td>C</td>
<td>20 μm</td>
<td>24 μm</td>
<td>2</td>
<td>Standard</td>
</tr>
<tr>
<td>D</td>
<td>30 μm</td>
<td>27 μm</td>
<td>3</td>
<td>Standard</td>
</tr>
</tbody>
</table>

Table 3.1 Sample Specification for Low Frequency Measurement

*Standard cure time is the cure time suggested by Ciba-Geigy Corporation and given in Chapter 2.

Figure 3.1 displays the variations in dielectric constant of Probimide 293 polyimide for samples A, B, C, and D as a function of frequency at room temperature. Each point in the figure represents the mean of measurements from at least two different sample structures. As in all appropriate succeeding plots, only some representative frequencies are shown for the sake of clarity. For both samples C and D the data indicates an invariant dielectric constant of 2.26 and 2.12, respectively, over the entire frequency range of 10Hz to 1MHz. For samples A and B, the data indicates a steady though slight decrease in $\epsilon_r$ with increasing frequency, i.e., from 2.34 at 10Hz to 2.30 at 1MHz for sample A and 2.38 at 10Hz to 2.35 at 1MHz for sample B.

The corresponding variations of dissipation factor with frequency at room temperature for the same samples are shown in Fig. 3.2. The data indicate that dissipation factor fluctuates between 0.0027 and 0.0036 for samples C and
Figure 3.1 Dielectric Constant of Probimide 293 vs. Frequency.
Figure 3.2 Dissipation Factor of Probimide 293 vs. Frequency.
D, whereas it increases with frequency from 0.0011 at 100Hz to 0.0030 at 1MHz for both samples A and B.

3.1.2 High Frequency Dependence

High frequency measurements in the range 1MHz to 1000MHz were performed on samples prepared from sheet method. As mentioned in Chapter 2, the polyimide sheets were obtained from both Ciga-Geigy and DuPont corporations, i.e., Probimide 293 and PI2555 and PI2545, respectively.

Six sample structures of different thicknesses were metalized following the metalization procedure given in Chapter 2. Table 3.2 illustrates the sample specifications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polyimide</th>
<th>Conductor Electrodes</th>
<th>Thickness</th>
<th>Obtained From</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Probimide 293</td>
<td>Silver Paint</td>
<td>1 mil</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>2</td>
<td>Probimide 293</td>
<td>Aluminum</td>
<td>1 mil</td>
<td>Ciba-Geigy</td>
</tr>
<tr>
<td>3</td>
<td>PI2555</td>
<td>Aluminum</td>
<td>0.8 mil</td>
<td>DuPont</td>
</tr>
<tr>
<td>4</td>
<td>PI2555</td>
<td>Aluminum</td>
<td>1.7 mil</td>
<td>DuPont</td>
</tr>
<tr>
<td>5</td>
<td>PI2545</td>
<td>Aluminum</td>
<td>1 mil</td>
<td>DuPont</td>
</tr>
<tr>
<td>6</td>
<td>PI2545</td>
<td>Aluminum</td>
<td>1.7 mil</td>
<td>DuPont</td>
</tr>
</tbody>
</table>

Table 3.2 Sample Specification for High Frequency measurements.

Figure 3.3 displays the variations in dielectric constant for Sample 1 as a function of frequency at room temperature. Each point in the figure represents the mean of measurements from three different sample structures. The
Figure 3.3 Dielectric Constant of Probimide 293 (Ag electrodes) versus Frequency.
data indicate a steady dielectric constant of 3.36 from 1 to 50MHz, and then a uniform decrease in $\varepsilon_r$ with increase in frequency, i.e., from 3.36 at 50MHz to 1.5 at 1GHz.

The corresponding variations of dissipation factor with frequency, at room temperature for Sample 1, are shown in Fig. 3.4. The data shows that dissipation factor increases with an increase in frequency from 0.0198 at 1MHz to 0.067 at 1GHz, with a peak of 0.072 at 700MHz.

Figure 3.5 displays the variations in $\varepsilon_r$ for Sample 2 with frequency. Each point in the figure represents the mean of measurements from four different sample structures. The data indicates a steady $\varepsilon_r$ of 3.20 from 1 to 150MHz and then a slight decrease in $\varepsilon_r$ with increase in frequency, i.e., from 3.20 at 150MHz to 2.76 at 1GHz.

The corresponding variations of dissipation factor with frequency at room temperature for Sample 2 are shown in Fig. 3.6. The data shows that dissipation factor increases with frequency from 0.0098 at 1MHz to 0.03 at 1GHz with a peak of 0.04 at 900MHz.

Figure 3.7 displays the variations in dielectric constant for Samples 3 and 4 with frequency at room temperature. Each point in the figure represents the mean of measurements from two different sample structures. The data displays a steady dielectric constant of 3.79 from 1 to 20 MHz and 1 to 180MHz for Samples 3 and 4, respectively, and then a uniform decrease in $\varepsilon_r$ with increase in frequency,
Figure 3.4 Dissipation Factor of Probimide 293 (Ag electrodes) versus Frequency.
Figure 3.5 Dielectric Constant of Probimide 293 (Al electrodes) versus Frequency.
Figure 3.6 Dissipation Factor of Probimide 293 (Al electrodes) versus Frequency.
Figure 3.7 Dielectric Constant of PI2555 vs. Frequency.
i.e., from 3.79 at 20MHz to 3.28 at 1GHz and from 3.79 at 180MHz to 3.51 at 1GHz, respectively.

The corresponding variations of dissipation factor with frequency at room temperature for the samples are shown in Fig. 3.8. The data indicates that dissipation factor increases with frequency from 0.009 and 0.007 at 1MHz to 0.008 and 0.007 at 1GHz with peaks of 0.033 at 500MHz and 0.028 at 600MHz for samples 3 and 4, respectively.

Figure 3.9 displays the variation in dielectric constant for Samples 5 and 6 with frequency at room temperature. Each point in the figure represents the mean of measurements from two different sample structures. The data exhibits an invariant dielectric constant of 3.45 and 3.75 at 1MHz to 200MHz for Samples 5 and 6, respectively, and then a uniform decrease in \( \varepsilon_r \) with increase in frequency; i.e., from 3.45 at 200MHz to 2.95 at 1GHz for Sample 5 and 3.75 at 200MHz to 3.45 at 1GHz for Sample 6.

The corresponding variations of dissipation factor with frequency at room temperature for the same samples are shown in Fig. 3.10. The data indicates that dissipation factor increases with frequency from 0.0057 and 0.0059 at 1MHz to 0.01 and 0.011 at 1GHz for Samples 5 and 6, respectively. Peaks of 0.02 at 500MHz for Sample 5 and of 0.022 at 700MHz for Sample 6 are also observed.
Figure 3.8 Dissipation Factor of PI2555 vs. Frequency.
Figure 3.9 Dielectric Constant of PI2545 vs. Frequency.
Figure 3.10 Dissipation Factor of PI2545 vs. Frequency.
3.2 Cure Time Dependence

Two samples were fabricated following the spin-on method. Probimide 293 polyimide was cured at half the suggested time (i.e., 85°C for 15 minutes, 150°C for 7.5 minutes, and 240°C for 7.5 minutes) on one set of samples, and on another set of samples the polyimide was cured at twice the suggested time (i.e., 85°C 1 hour, 150°C for 30 minutes, and 240°C for 30 minutes).

Low frequency measurements were performed on the samples described above. Table 3.3 illustrates the sample specifications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target Thickness</th>
<th>Measured Thickness</th>
<th>Number of Layers</th>
<th>Cure Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>10 µm</td>
<td>11 µm</td>
<td>2</td>
<td>1/2 Standard</td>
</tr>
<tr>
<td>F</td>
<td>10 µm</td>
<td>10 µm</td>
<td>2</td>
<td>2 x Standard</td>
</tr>
</tbody>
</table>

Table 3.3 Sample Specification for Cure-Time Dependence

Figure 3.11 displays the variations in dielectric constant of both Samples E and F with frequency at room temperature. Each point in the figure represents the mean of measurements from at least two different sample structures. For both Samples E and F the data indicates an invariant dielectric constant of 2.45 and 2.16, respectively, over the entire frequency range.

The corresponding variations of dissipation factor with frequency at room temperature for the same samples are
Figure 3.11 Dielectric Constant of Probimide 293 vs. Frequency.
shown in Fig. 3.12. The data indicates that dissipation factor increases linearly with frequency, from 0.0025 and 0.0010 at 100Hz to 0.0035 and 0.0020 at 1MHz for Samples E and F, respectively.

3.3 Thickness Dependence

Table 3.4 shows the thickness variations in dielectric constant at room temperature for Probimide 293, PI2545 and PI2555 at a frequency of 1MHz. The data indicates an increase in dielectric constant for PI2545 from 3.45 at a thickness of 1 mil to 3.75 at a thickness of 1.7 mils, whereas it stays constant for PI2555. For Probimide 293, the data indicates that $\varepsilon_r$ decreases with thickness.

<table>
<thead>
<tr>
<th>Polyimide</th>
<th>Thickness</th>
<th>Dielectric Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probimide 293 (Spin-on)</td>
<td>10 $\mu$m</td>
<td>2.34</td>
</tr>
<tr>
<td>Probimide 293 (Spin-on)</td>
<td>24 $\mu$m</td>
<td>2.26</td>
</tr>
<tr>
<td>Probimide 293 (Spin-on)</td>
<td>27 $\mu$m</td>
<td>2.12</td>
</tr>
<tr>
<td>Probimide 293 (Sheet)</td>
<td>1 mil</td>
<td>3.20</td>
</tr>
<tr>
<td>PI2545</td>
<td>1 mil</td>
<td>3.45</td>
</tr>
<tr>
<td>PI2545</td>
<td>1.7 mil</td>
<td>3.75</td>
</tr>
<tr>
<td>PI2555</td>
<td>0.8 mil</td>
<td>3.79</td>
</tr>
<tr>
<td>PI2555</td>
<td>1.7 mil</td>
<td>3.79</td>
</tr>
</tbody>
</table>

Table 3.4 Dielectric Constant Variations with Thickness
Figure 3.12 Dissipation Factor of Probimide 293 vs. Frequency.
3.4 Temperature Dependence

The temperature dependence of the dielectric constant was measured at frequencies of 500KHz and 1MHz using the low frequency impedance analyzer described in Chapter 2. Samples A, C, and D, described in Section 3.1.1, were heated, using a hot plate, from room temperature up to 215°C. A thermocouple was used to measure temperature difference between top and bottom of sample. A difference of ±3°C was measured for high temperature (>180°C), whereas a difference of less than 1°C was measured for lower temperatures.

Figure 3.13 displays variations in dielectric constant of the three samples. Each point in the figure represents the mean of measurements of two different sample structures. For Sample A, the dielectric constant remained constant at 2.41 up to 80°C, and then it decreased with temperature to a value of 2.27 at 215°C. For Sample C remained constant at 2.30 up to 94°C and then it decreased with temperature to a value of 2.24 at 215°C, whereas for Sample D, ε_r remained constant at 2.22 up to 90°C and then decreased with temperature to a value of 2.15 at 215°C.

3.5 Electrode Composition and Thickness Analysis

Aluminum thickness determined by RBS was measured to be 3852 ± 112 Å. Figures 3.14 and 3.15 are RBS plots of
Figure 3.13 Dielectric Constant of Probimide 293 vs. Temperature.
Figure 3.14 RBS plot of Aluminum on Carbon.
Figure 3.15 (blow up) of RBS plot of Aluminum on Carbon.
aluminum on carbon, which also give no indication of any measurable impurities.

In the following chapter a detailed discussion of the results will be presented.
CHAPTER 4

DISCUSSION

Experimental results related to (1) low and high frequency dependence of dielectric constant and dissipation factor of Probimide 293, PI2545 and PI2555 polyimides at room temperature; (2) temperature dependence of and D of Probimide 293 polyimide in the low frequency range; and (3) thickness dependence of εr and D of Probimide 293 polyimide in the low frequency range are discussed sequentially in the following section, preceded by a general introduction to the dielectric properties of polymers.

Dielectric Properties of Polymers

In general, the dielectric constant of a polymeric material varies with temperature, frequency, structure, and atomic bonding. Induced or permanent electric dipoles in the dielectric are influenced by all these factors.

The field actually experienced by a molecule situated inside a dielectric material sandwiched between two charged conductor plates is known to be greater than the applied electric field E. This is due to the polarization which occurs in the dielectric. There are two major types of polarization processes that occur in homogeneous polymeric materials, namely: (1) electronic polarization which is
caused by the shift of the center of the negative electron cloud of each atom from its positive nucleus; and (2) orientation polarization which is present in the case of materials that have asymmetric molecules whose permanent dipole moments can be aligned by the electric field. The total polarizability of the dielectric is the sum of these polarization sources (8). Fig. 4.1 displays frequency ranges over which different polarization mechanisms operate in a typical dielectric. (Note that the space change and ionic polarization processes are not present in homogeneous polymeric materials.)

**Figure 4.1** Schematic Diagram of Variation of Dielectric Properties for a Material Having Electronic, Atomic, Orientation and Space Charge Polarizations (8)
One or a combination of these polarizations is always present at a particular temperature or frequency of applied field and thereby plays a major role in characterizing the material's properties (6).

The dielectric constant in an alternating field depends on the flexibility with which the dipoles can reverse alignment with each reversal of the field. The time required to achieve this reversal (i.e., to reach equilibrium orientation) is called the relaxation time, and its reciprocal, the relaxation frequency. When the frequency of applied field exceeds that of the relaxation frequency of a certain polarization process, the dipoles cannot reorient themselves fast enough, which terminates the operation of the process. Since the relaxation frequencies of the different polarization processes differ, it is possible to determine their contributions to the dielectric constant and dissipation factor experimentally, as seen in Fig. 4.1.

The effect of temperature on the dielectric constant of a polymeric material is, in general, small at low temperatures but increases with increasing temperatures. At high temperatures disorientation of dipoles takes place, resulting in a decrease of polarization, which leads to a decrease in dielectric constant.

Similarly, energy losses (i.e., dissipation factor) that occur in dielectrics are due to d-c conductivity and dipole relaxation. Moreover, the number of CO groups per
unit volume present in polymers also affects the dissipation factor as temperature varies. Usually a maximum loss tangent occurs when the frequency of the applied field equals the relaxation frequency, that is, when resonance occurs (6).

With the brief description given above, we can proceed to the discussion of the results obtained in Chapter 3.

4.1 Frequency Dependence

Following the procedure of Chapter 3, frequency dependence will be divided into two groups: low and high frequency dependence.

4.1.1 Low Frequency Dependence

According to the Ciba-Giegy Corporation data sheet, the dielectric constant of Probimide 293 polyimide is 3.3 at a frequency of 1KHz, with a dissipation factor of 0.003 at the same frequency. However, no reference was made to the method of sample preparation, that is, the spin-on or sheet method. Figures 3.1 and 3.2 show data taken on Ciba-Geigy's spin-on Probimide 293 polyimide. The average value of the dielectric constant of all four samples A, B, C, and D was found to be 2.29 at 1KHz, with an average dissipation factor of 0.0025 at 1KHz. Correlation between dielectric constant and dissipation factor measurements to that reported by Ciba-Giegy was 31% and 17%, respectively. The differences, however, appear to be more a function of sample preparation rather than a fundamental material's cause. Further
discussion of this discrepancy will be presented in the next section.

Taking a closer look at Fig. 3.1, which displays the dielectric constant versus frequency of samples A, B, C and D, four different values of \( \varepsilon_r \) for the same Probimide 293 polyimide were measured. A difference of 10% between worst cases (i.e., samples B and D) is found. This difference appears reasonable within experimental error. Hence, no thickness dependence could be inferred.

In summary, it is concluded that Probimide 293 has a constant \( \varepsilon_r \) over the frequency range of 10Hz to 1MHz, and no polarization effects were observed, as confirmed by the invariant \( \varepsilon_r \) and D over that frequency range.

4.1.2 High Frequency Dependence

High frequency measurements were performed on the sheet method samples 1, 2, 3, 4, 5 and 6. As illustrated in Table 3.2, both samples 1 and 2 are Probimide 293, with silver conductive paint and aluminum electrodes, respectively. Comparing both figures 3.3 and 3.5 for samples 1 and 2, the dielectric constants are 3.36 and 3.20 at a frequency of 1MHz, respectively. This yields a difference of 5% for the same polyimide. This difference is consistent within experimental error.

Averaging the data for this set of measurements and comparing it to the reported Ciba-Geigy value of 3.3
(assuming that at 1MHz is also 3.3) we get a difference of 0.6%. Such agreement indicates that the reported values from Ciba-Giegy were probably for sheet samples.

The large difference in \( \epsilon_r \) values between the spin-on and sheet samples is most likely due to the difference in solids content. Solids contents can dramatically affect the value of the dielectric constant. The sheet Probimide 293 has a substantially higher solids content than the spin-on Probimide 293, which is necessary to attain the greater thickness without significant distortion. Per Ciba-Geigy, the higher the solids content, the higher the dielectric constant.

Sample 2 also has a dielectric constant of 2.76 at 1GHz, corresponding to a difference of 14%, whereas Sample 1 has a dielectric constant of 1.5 at 1GHz, which corresponds to a difference of 55%. This dramatic change in the dielectric constant of Sample 1 is probably an artifact due to loss of adhesion of the silver paint to the polyimide at the higher frequencies, which results in trapping a layer of air between polyimide and the conductors. This places the air in parallel with the polyimide, thus yielding an effective dielectric constant equal to

\[
\frac{1}{\epsilon_r} = \frac{V_1}{\epsilon_1} + \frac{V_2}{\epsilon_2}
\]

(4.1)

where \( V_1 \) and \( V_2 \) are the volume fractions of the polyimide and air layer, respectively, and \( \epsilon_1 \) and \( \epsilon_2 \) are their respective dielectric constants. Since \( \epsilon_2 = 1 \), \( \epsilon_r \) will be less,
Sample 2, which has aluminum metalization, did not exhibit this sharp decrease in dielectric constant because (1) aluminum adhesion is excellent to polyimide, and (2) aluminum used was pure, as verified by the RBS results shown in Figures 3.14 and 3.15.

Figures 3.4 and 3.6 give the dissipation factor of both samples. Two peaks of 0.072 at 700 MHz and 0.04 at 900 MHz are measured for samples 1 and 2, respectively. This translates to an increase of 260% for Sample 1 and 300% for Sample 2. This increase in dissipation factor is probably due to the orientation polarization processes present at those frequencies (as displayed in Fig. 4.1).

Comparing Figures 3.7 and 3.9 for samples 3, 4, 5 and 6, it is noticed that the dielectric constant of all samples decreases with frequency. For example $\varepsilon_r$ decreases 13% for Sample 3, 7% for Sample 4, 14.5% for sample 5, and 8% for Sample 6 over the entire frequency range. This decrease in $\varepsilon_r$ is most likely due to a decrease in the orientation polarization contributions (see Fig. 4.1) which is typically found in this frequency range. Similarly, for Figures 8 and 10 which give the dissipation factor of those samples, peaks are measured between 700MHz to 900MHz, and this is probably due to orientation polarization.
4.2 Temperature Dependence

Figure 3.13 shows the variation of dielectric constant for Samples A, C and D versus temperature. The full-cured samples were heated for 6 to 10 minutes before each reading was taken. In all samples, the dielectric constant remained unchanged up to 80°C and then started decreasing slightly as the temperature increased. The dielectric constant of Sample D decreased about 3% from 80°C up to 215°C, whereas \( \varepsilon_r \) for sample A decreased about 6% over the same temperature range. This decrease in dielectric constant is expected because at higher temperatures disorientation of dipoles is appreciable and the orientation polarization contribution decreases.

4.3 Thickness Dependence

Of the measurements taken on samples of different thicknesses, the decrease in \( \varepsilon_r \) appears to be an inverse function of the sheet thickness. For example, the dielectric constant of Sample 3 decreased by 13% over the frequency range of 1MHz to 1GHz, whereas \( \varepsilon_r \) decreased by 7% for Sample 4 over the same frequency range, and, similarly, 14.5% and 8% for Samples 5 and 6, respectively. Because of stresses that cause significant distortion within the sheet, the maximum flat layer of polyimide that could be fabricated was 1.7 mils for the DuPont material and 1 mil for the Ciba-Geigy polyimide. Although the results suggest a possible
thickness effect, there is no clear evidence to support this statistically. Moreover, the 13%, 7%, 14.5% and 8% decrease in \( \varepsilon_r \) displayed by Samples 3, 4, 5 and 6 could be accounted for by experimental errors such as (1) the errors associated with the resolution, sensitivity and calibration of the instrument, and (2) the errors involved in sample preparation. For example, the measurement resolution and accuracy of each instrument depends on the measuring frequency and the necessary calibrations which are performed under automatic settings of both instruments. The basic accuracy of the instrument is about 1 to 3%. Nevertheless, factors such as ambient temperature and cable length may increase the error limits (9).

As no change of dissipation factor was noticed in thicker samples, results show that dissipation factor is independent of film thickness.

4.4 Cure-Time Dependence

A comparison between a half-cured sample and a twice-cured sample is shown in Fig. 3.11. Sample E, which is cured one-half the suggested time, has a dielectric constant of 2.45, which is 14% greater than that of Sample F, which was cured at twice suggested time, and 7% greater than that of standard cure. The dissipation factor in E is also 150% higher than the dissipation factor of F at 1KHz. Hence, the results show that dielectric constant of a fully
cured sample is less than that of a half-cured sample, and, similarly, for the dissipation factor, which is due to incompleteness of formation of the final stage of polyimide (4).

4.5 **Compatibility with Multilayer Interconnect Structures**

The increase in signal speeds and integrated circuit complexity has created the need for higher density interconnections to accommodate the larger numbers of input-output signals. This demand for high interconnect density necessitates multilayer structures.

Polyimide proves to be an excellent dielectric for use in multilayer interconnect structures because it has a low and virtually constant $\varepsilon_r$ over a wide frequency range.

Figure 4.2 shows a schematic of a typical multilayer copper/polyimide interconnection structure used in the packaging of highly complex integrated circuits (7). The ceramic substrate provides power and ground wiring to the IC's and contains pins or pads to the next level packaging. Copper conductor lines are deposited and patterned between layers of polyimide, providing combinations of microstrips and striplines for chip interconnection.

Both Ciba-Geigy's and DuPont's polyimides are excellent for use in such multilayer structures; however, results obtained in this study show that Probimide 293 has a lower dielectric constant than both PI2545 and PI2555, indicating that it might be preferred for high frequency application.
Figure 4.2 Typical Package for Multilayer Interconnection Structure
CHAPTER 5

CONCLUSION

Dielectric constant and dissipation factor of commercially available polyimides (i.e. Ciba-Geigy's Probimide 293 and DuPont's PI2545 and PI2555) were measured as a function of deposition condition, measurements condition, frequency, and temperature.

A dielectric constant of 3.20, 3.79, and 3.60 at a frequency of 1MHz was measured for all Probimide 293, PI2555 and PI2545 polyimide sheets respectively. Those values remained relatively constant up to a 1GHz frequency. A dissipation factor of about 0.01 at 1MHz was measured for all polyimides, and this value remained invariant up to 200 MHz. Dissipation factor of as high as 0.07 was measured between the frequency range of 200 MHz to 1GHz.

An average value of 2.29 was measured for the dielectric constant of the spin-on Probimide 293. This value remained invariant up to a 1MHz frequency at room temperature. The corresponding average value of dissipation factor was about 0.003 over the same frequency range 10Hz to 1MHz.

Dielectric constant of a half cured sample was found to be 14% higher than the value obtained for a fully cured
sample. However, a dissipation factor of 150% higher was measured for the same sample.

The dielectric constant of the spin-on Probimide 293 was also measured at 500KHz and 1MHz frequencies and found to be 2.29 up to 80°C temperature. This value of 2.29 decreased about an average of 4% as temperature was increased to a value of 215°C.

These results suggest that the polyimides meet electrical property requirements for use in high speed, high interconnect density multilayer structures.

More work and research, however, still needs to be done on polyimides, namely, (1) the high frequency dielectric properties of polyimide at high temperatures, (2) the effect of moisture absorption of polyimide films on dielectric properties of polyimide, (3) the effect of the stresses introduced by the fabrication process on the dielectric properties of polyimide, and (4) the effect of solids content in polyimides on the dielectric properties.
REFERENCES


5. ASTM, Designation: D 150-81.


9. HP 4191A RF Impedance Analyzer Manual

SELECTED BIBLIOGRAPHY

Though these entries are not cited in the text, they are included in this section for the convenience of the reader in obtaining further information of a detailed or explanatory nature.


"Basic Integrated Circuit Engineering." Hamilton and Howard.


"Laboratory Manual for Integrated Circuit Technology." Microelectronics Lab Staff, University of Arizona.


