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Properties of Thin Polyimide Films

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ABSTRACT

Polyimide is receiving increasing interest as a possible insulator on semiconductor devices, replacing SiO₂. Several commercially available polyimides have been characterized by testing films of them for electric breakdown strength, conductivity, adhesion, and other properties. The results of these tests are summarized, and the polyimides are compared to sputtered SiO₂.

Polyimide has excellent thermal stability and chemical resistance, along with good dielectric properties. This combination of characteristics makes it promising as a replacement for SiO₂ for insulating semiconductor devices. Several multilevel metal structures using polyimide as the insulator have been described in the literature (1-4).

To develop a base of understanding in support of this use of polyimide, several commercially available materials have been tested for a variety of functional properties. Film thickness ranged from 1 to 3 μm. Electrical and physical measurements were compared with measurements for sputtered SiO₂ films.

Sample Preparation

A description of the polyimide materials as received from the vendor is shown in Table I. There are considerable differences in these materials, including solvent system, solids content, and viscosity. Two of the materials were received in powder form, which is an advantage in terms of shelf-life. The materials received in solution, such as polyamic acid, had a shelf-life of approximately one year when stored at 4°C.

In order to cast films of 1-3 μm thickness by spin coating, the materials were diluted with additional solvent to the solids content shown in Table I. It is interesting that there is also a difference in the solids content of the solutions for coating the same film thickness. As received, all the materials had a great deal of particulates and, therefore, all the solutions had to be filtered prior to use. Filtering was done using silver membrane filters with a pore size of 0.45 μm. Thin films of 1-3 μm were prepared by spin coating at spin speeds of 4-6 krpm. Curing was done on hot plates. All of the testing was done on blanket polyimide films.

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Key words: electric breakdown strength, conductivity, adhesion, insulators.

Table I. Comparison of various polyimide resins as received and as used

Polyimide	As received			As used
	Solids content (w/o)	Viscosity (cps)	Solvent	Solids content (w/o)
A	16	6000	NMP	13
B	27	5600	NMP/acetone	18
C	38-42	250-350	DMF	32
D	63-67	3000-7000	NMP	47
E	55	4000	NMP/methanol	36
F	Powder		4:1	60
G	Powder			15

NMF: methylpyrrolidinone.
DMF: dimethylformamide.

Dielectric Properties

In order to use polyimide as a replacement for SiO₂ for insulating semiconductor devices, it must have good dielectric properties. Measurements of breakdown strength, conductivity, dielectric constant, and the dissipation factor have been made on fully cured polyimide films with comparisons made to sputtered SiO₂.

The cure cycle was determined by dissipation factor measurement, as suggested by Gregoritsch (5). An Al-polyimide-Al dot structure was used and the dissipation factor was measured at a frequency of 1 MHz, as a function of the final cure temperature. Some results are shown in Fig. 1a and b. The dissipa-

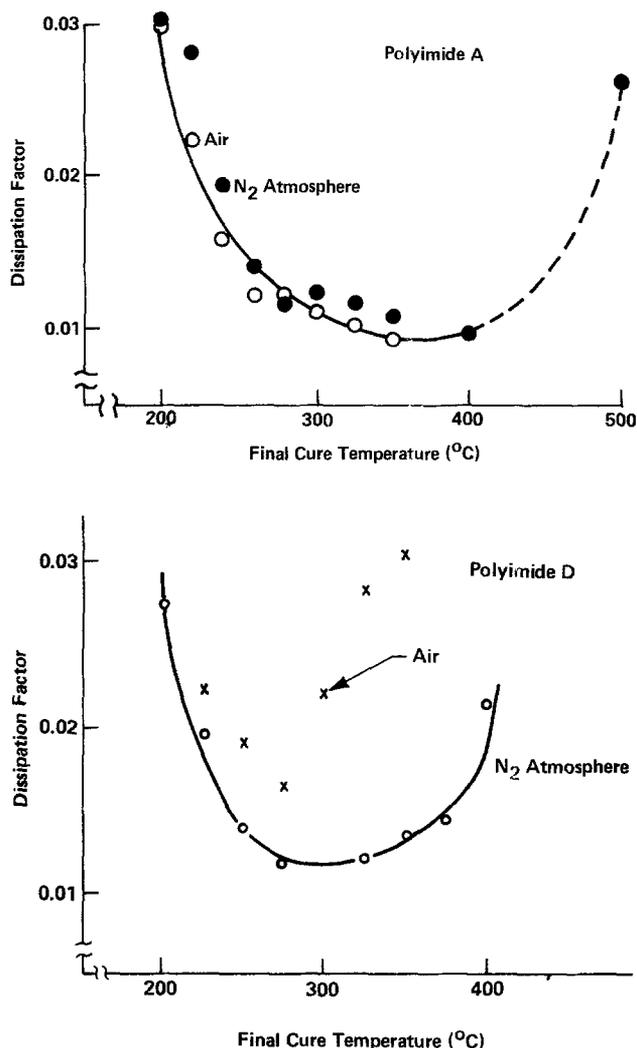


Fig. 1. Dissipation factor as a function of final cure temperature for (a) 1.5 μm film of Polyimide A, (b) 1.5 μm films of Polyimide D. Time at final cure temperature was 30 min.

tion factor decreases with increasing cure temperature until full cure is reached and then increases as decomposition starts to occur. Curing in nitrogen and air were investigated. Figure 1b shows that for Polyimide D there is a substantial difference in the dissipation factor between curing in air and nitrogen whereas Polyimide A does not exhibit this effect. For the data which follows, the curing of the polyimides was therefore done in a nitrogen atmosphere for the final cure. The dissipation factor of the fully cured 1.5 μm polyimide films was approximately 0.01 for all the materials tested.

The dielectric breakdown strength was measured using an Si-polyimide-Al dot structure. The polyimide film thickness used was 1.5 μm . Al dots of 1.5 mm diam were used. Fifty measurements were made on each wafer. The voltage was ramped at a rate of 1 V/sec until breakdown occurred. It can be seen in Table II that all of the polyimide films tested exhibited good dielectric breakdown strength, which is comparable to SiO_2 . The data reported in Table II are for polyimide films cast from carefully filtered solutions as described previously. Without filtering the raw materials the dielectric breakdown strength was in the low 10^5 V/cm range.

For measurements of conductivity, an Al-polyimide-Al dot structure was tested in electric fields ranging from 5×10^4 to 5×10^5 V/cm and temperatures up to 250°C. Figure 2 shows that the log of the resultant current varies linearly with the square root of the electric field for all of the materials tested. This exponential dependence of the current on the square root of the applied voltage has been reported previously for Kapton polyimide films (6). It is observed in Fig. 2 that the conductivities of individual polyimides differ widely, and all of them are considerably higher than that of sputtered SiO_2 . All of these materials, however, appear to be adequate insulators, since for typical semiconductor device use conditions (85°C, 10^5 V/cm) their resistivities are over 10^{12} $\Omega\text{-cm}$.

Data is not presented for Polyimide F due to problems of instability in the film, probably due to water absorption. The films of Polyimide F would appear quite conductive ($J > 10^{-3}$ A/cm²) as initially tested. After baking the test samples for an hour at 200°C and then immediately testing, the conductivity of the films was similar to the other polyimide films. If the test sample remained at ambient conditions for a few hours, it would become conductive once again. This phenomenon was not observed with any of the other materials.

The dielectric constant was measured at a frequency of 1 MHz and found to be approximately 3.5 for all of the polyimide films tested compared to 3.8 for sputtered SiO_2 . This lower dielectric constant of polyimide is an advantage over SiO_2 .

Planarization

For high density multilevel metal-insulator structures it is desirable to have a planar surface. It has been reported in the literature (1, 2) that polyimides can be used as the insulator to provide such a planar structure. During the cure cycle for the polyimide film there is a tendency for flow to occur. Also, during

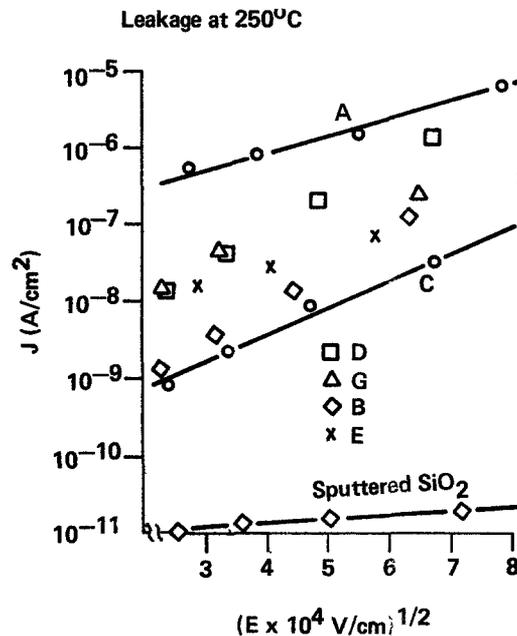


Fig. 2. Current density vs. applied field at 250°C for various polyimide films with a comparison to sputtered SiO_2 .

the cure cycle there is a great deal of shrinkage due to solvent loss. It was observed that some of the materials tested exhibited a combination of less shrinkage and more flow than others. It is the combination of shrinkage and flow during the three stages of the cure cycle which provides polyimide films with the ability to planarize or smooth out any topological structures on a substrate.

The degree of planarization is determined by the ratio of the step height resulting with the polyimide film to the initial step height of the metal pattern as shown in Fig. 3. Another factor in the degree of planarization is the slope of the resulting step.

The planarity measurements were made with a Taylor-Hobson Talystep and also SEM examination. Some general observations for all the polyimide films are that the degree of planarization is directly dependent on the thickness of the polyimide films. The slope of the polyimide over the metal land decreases with increasing polyimide thickness. It was also observed that the degree of planarization is dependent on both the width and spacings of the metal lines which the polyimide is covering as shown in Fig. 4. Thin lines with narrow spaces result in better planarization. Unfortunately, this geometry dependence of planarization becomes quite complicated since a group of closely spaced lines, separated by a large distance (≥ 12 μm) from other lines, act as one wide land. However, it seems that a group of narrow lines planarizes slightly better than a single line of the same overall width. The degree of planarization, therefore, is dependent on the geometry of the

Table II. Dielectric breakdown strength of 1.5 μm polyimide films

Polyimide	Average breakdown field ($\times 10^6$ V/cm)
B	4.74
D	5.62
A	5.94
G	6.28
E	6.63
C	7.06
F	7.50
SiO_2 (sputtered)	8.60

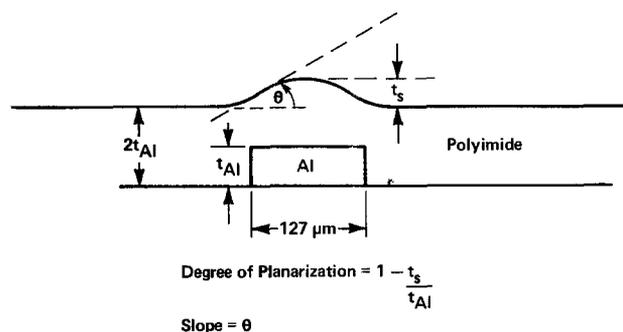


Fig. 3. Degree of planarization for polyimide over a metal step

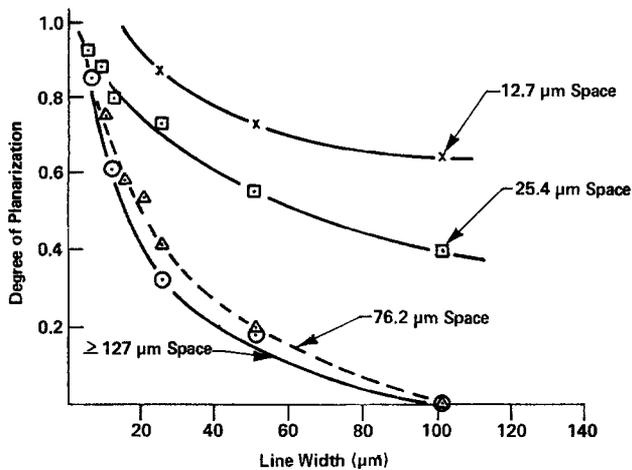


Fig. 4. Planarization as a function of line width and space for Polyimide C films.

metallization pattern (*i.e.*, individual line widths, line spacings, and group dimensions).

A difference in the degree of planarization was observed for the various materials tested. Figure 5 shows Talystep measurements for two polyimides over a metal pattern of varying line widths. The trend toward more planarization as the line width decreases is seen for both materials; however, in general, Polyimide C planarizes more than Polyimide A. Figure 6 illustrates the difference in planarity of the two materials. In order to make an easy comparison of planarization, measurements were made over a single metal line of 12.7 μm in width. Table III shows the degree of planarization for the various polyimide films. Three of the materials seem to provide a conformal type coating, while the other four polyimides seem to planarize more. There appears to be a correlation between the solids content of the coating solution and the degree of planarization. Higher solids content material provides more planarization.

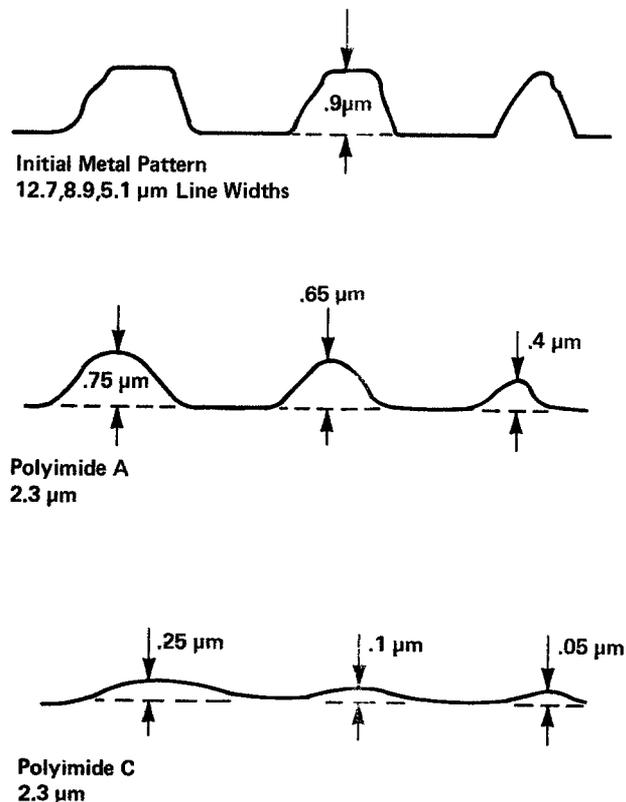


Fig. 5. Talystep measurements comparing degree of planarization achieved with Polyimide A and Polyimide C films.

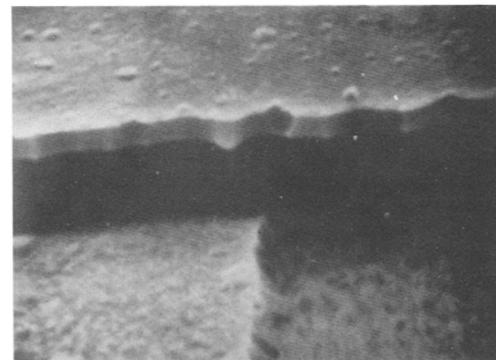
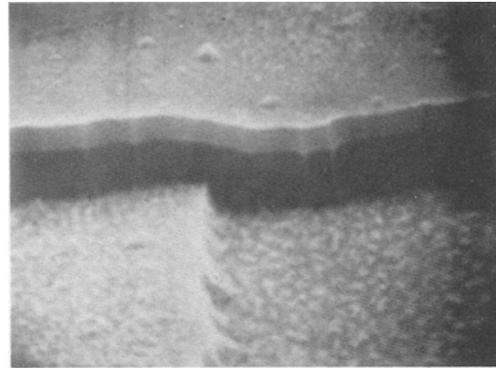


Fig. 6. SEM pictures compare the degree of planarization of Polyimides A (top) and C (bottom). Pictures show a cross section of a polyimide film (which is covered with Al) over a metal line. (The cross section was made by RIE and the Al over the polyimide was used as a mask). (6000 \times .)

Due to the many geometry effects, it does not seem possible to completely planarize a typical metal pattern with a polyimide film. Good edge coverage, however, is obtained with all of the various polyimide films even when planarization is not achieved. This good edge coverage of polyimide films is an advantage over standard sputtered SiO_2 films deposited with a re-emission coefficient of ~ 0.3 (7). Typically SiO_2 films are somewhat conformal but have a tendency to cusp at the edges of metal lines resulting in poor edge coverage.

Adhesion

One of the most important properties of a thin film, such as polyimide, is its adhesion to the semiconductor substrate and metallurgy, and the adhesion of other materials to the polyimide film. Of the numerous methods for the measurement of adhesion of thin films (8), the technique we found the most reliable was the peel force test.

A schematic of the peel force test apparatus is shown in Fig. 7. The force transducer is fixed on a sliding stage. It is connected by a long rod to the test sample. The test sample consists of a strip of wafer of known width attached by two sided tape to a glass slide. It is mounted such that approximately

Table III. Degree of planarization for 2 μm polyimide films over 1 μm Al lines

Polyimide	% of solids in solution used to coat 2 μm film	Degree of planarization (over 12.7 μm line)
A	13	0.17
B	18	0.30
G	15	0.32
C	32	0.72
D	47	0.78
E	36	0.78
F	60	0.82

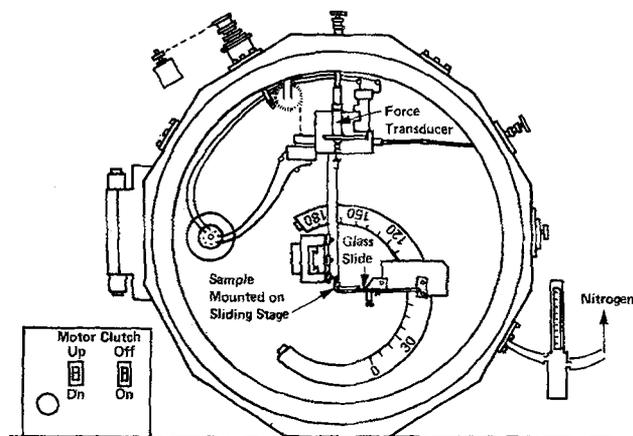


Fig. 7. Schematic of peel force test apparatus

a quarter inch of the wafer strip overhangs the edge of the glass slide. The wafer strip is carefully broken where it overhangs the glass slide, leaving the film intact. Then this part is bent up and attached to the flat end of the rod using glycolphalate. The stage was adjusted for a peel angle of 90° for consistency and ease of peeling. The peel rate is 0.15 mm/sec. The stage holding the test sample slides at the same rate as the stage holding the force transducer providing a constant peel angle. The output of the force transducer is recorded on a strip chart recorder. The peel test is performed in an enclosed chamber which is purged with dry nitrogen.

Strips of wafers of various widths were used to obtain a relative measure of adhesion. A graph of peel force vs. width as shown in Fig. 8 is plotted and the slope of this line (*K*) is used as the relative measure of adhesion. It is also observed that the intercept of this line is not always zero due to edge effects: damage inflicted to the interface at the edges while the wafers were scribed into strips.

Adhesion measurements were made after processing and again after temperature-humidity stress cycles.

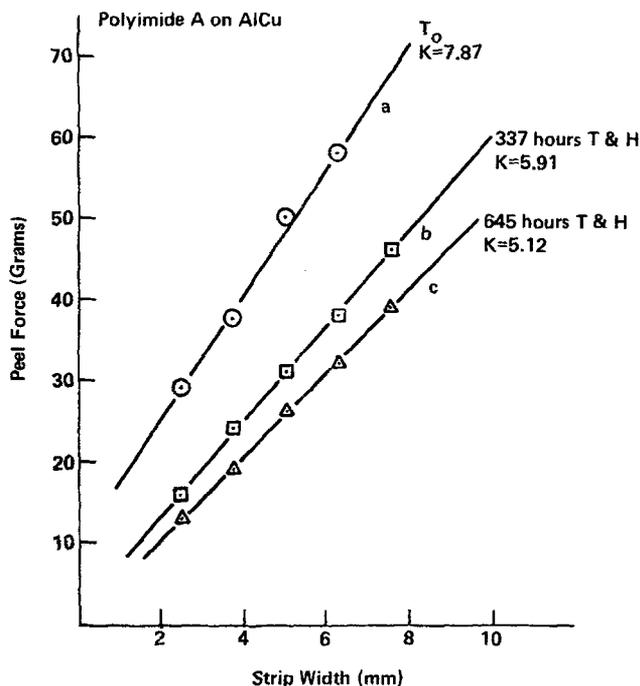


Fig. 8. Peel force vs. strip width for Polyimide A on AlCu, as a function of time in a temperature/humidity chamber. (a) initially *K* = 7.87 g/mm, (b) after 337 hr at 85°C, 80% relative humidity *K* = 5.91 g/mm, (c) after 645 hr *K* = 5.12 g/mm.

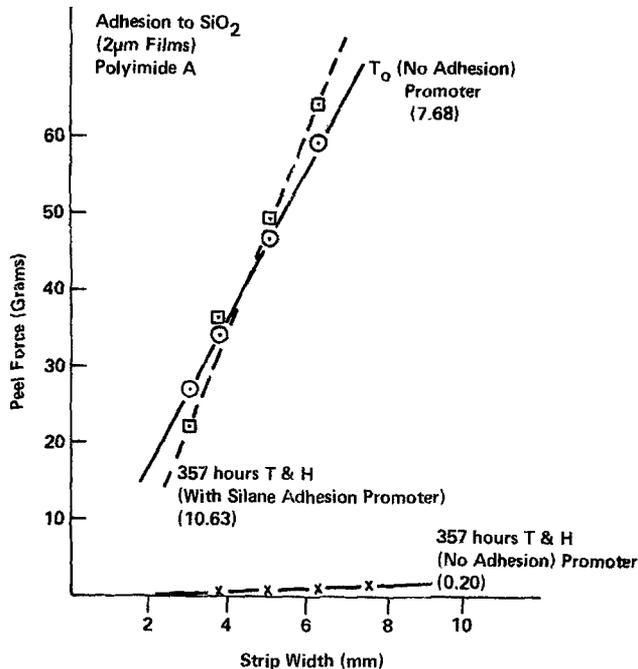


Fig. 9. Polyimide adhesion to SiO₂. Using silane adhesion promoter: No peel at T₀ and *K* = 10.63 g/mm after 357 hr at 85°C, 80% relative humidity. Without any adhesion promoter: *K* = 7.68 at T₀ and *K* = 0.20 g/mm after 357 hr of T&H.

Figure 8 shows that the adhesion tends to degrade after exposure to temperature-humidity stressing.

The initial adhesion of polyimide to Si and SiO₂ surfaces was good; long exposure to stressing, however, tended to degrade the interface. It was found that silane adhesion promoters (9) improved the long-term stability of the bond. Figure 9 shows a comparison for Polyimide A on SiO₂. Both at T₀ and after stressing the adhesion of the polyimide film to SiO₂ is improved when a silane-type adhesion promoter was used.

It is observed in Table IV and Fig. 8 that the major degradation in the adhesion appears after the initial exposure to T&H stressing.

The "no peel" condition shown in Table IV indicates excellent adhesion. It occurs when the peel starts and a full scale deflection is recorded on the chart recorder and the polyimide film tears, thereby implying a peel factor of 31.5 g/mm or greater. A partial peel condition is more difficult to interpret. This is when the polyimide film starts to tear unevenly as it is peeling, indicating that the adhesion of the film is not uniform across the surface, and that there are areas of very good adhesion where the polyimide film is not peeling.

For all the data presented a silane adhesion promoter was used on Si and SiO₂ surfaces. However, for Al surfaces no difference was found in the adhesion of polyimide with or without an adhesion promoter.

Table V illustrates that the adhesion at T₀ of polyimide to Si is good for all the materials tested. After T&H stressing, however, two of the materials show a degradation in their adhesion to Si surfaces.

Table IV. Polyimide adhesion to SiO₂ as a function of temperature and humidity stressing at 85°C, 80% relative humidity

Polyimide	Adhesion to SiO ₂ : <i>K</i> (g/mm) hr T&H					
	T ₀	357	762	1122	1770	2495
A	PP	11.03	9.06	10.24	6.70	8.27
B	NP	NP	NP	NP	NP	NP

NP: no peel, excellent adhesion. T&H: 85°C, 80% relative humidity. 2 μm polyimide films.

Table V. Polyimide adhesion to Si

Polyimide	Adhesion to Si: K (g/mm)	
	T ₀	After 563 hr T&H
F	NP	NP
D	NP	NP
C	NP	NP
G	PP	8.67
E	NP	NP
A	NP	18.52
B	NP	NP

3 μm polyimide films on Si wafers.
 NP: no peel condition, excellent adhesion ≥ 31.52 g/mm.
 PP: partial peel, films start to peel unevenly then tear.
 T&H: 85°C, 80% relative humidity.

The adhesion of polyimide films over Al and Al alloys was excellent for almost all the materials tested as shown in Table VI. The adhesion of Al over polyimide was satisfactory before the T&H stress cycle, but severely degraded after it for all materials tested. Typically, values of K greater than 18 g/mm were measured at T₀; however, after 200 hr at 85°C, 80% relative humidity, the value of K went down below 3 g/mm. Annealing the metal at 350°C in nitrogen before test improves the Al to polyimide adhesion,

Table VI. Polyimide adhesion to Al

Polyimide	Adhesion to Al: K (g/mm)	
	T ₀	After 564 hr T&H
F	NP	NP
D	NP	NP
C	PP	PP
G	PP	PP
E	NP	NP
A	10.64	8.27
B	PP	PP

3 μm polyimide films of Al surface without using any adhesion promoter.
 T&H: 85°C, 80% relative humidity.
 NP: no peel condition, excellent adhesion ≥ 31.52 g/mm.
 PP: partial peel, film starts to peel unevenly then tears.

resulting in a peel factor of approximately 10 g/mm after the stress cycle.

Conclusion

In summary, the polyimide films of various vendors exhibited differences in functional properties. The dielectric properties of polyimide films are not quite as good as sputtered SiO₂ with regard to breakdown strength and resistivity. The adhesion of polyimide to various materials is also not always as good as SiO₂ depending on the polyimide. Polyimide does provide an advantage in good edge coverage and some planarization of topography. Considering all of these properties, polyimide films seem to be more than satisfactory for application to semiconductor devices.

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The Dependence of the Memory Effect in ZnS:Mn A-C Thin Film Electroluminescence on Mn Distribution

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ABSTRACT

It is known that the width of the memory loop of the brightness-voltage characteristic in ZnS:Mn a-c thin film electroluminescence devices depends on the Mn doping concentration and on the ZnS:Mn film thickness. In this study we have varied the ZnS thickness fraction doped with Mn and its location. The results of this study show that the memory loop widens incrementally with the ZnS thickness fraction doped with Mn. We infer that the Mn doping is affecting the high-field bulk conductivity of the ZnS.

The "memory effect" in ZnS a-c thin film electroluminescence (EL) is related to the Mn doping of the ZnS (1). In addition, studies have shown that the width of the "memory loop," i.e., the width of the hysteresis in the brightness-voltage characteristic, is a function of the Mn doping concentration (2, 3)

Key words: electroluminescence, ZnS:Mn, thin film device.

and the ZnS:Mn film thickness (3, 4). The Mn doping can influence the memory effect by affecting the bulk conductive properties of the ZnS and or by introducing electronic trapping states near the ZnS-dielectric interface. The purpose of this study was to determine the relative importance of these effects on the "memory effect."