Gravimetric Measurements of Steady-State Moisture Uptake in Spin-Coated Polyimide Films

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SYNOPSIS

Polyimide (PI) is an insulating polymer that is finding increased use in the semiconductor industry as an intermetal dielectric, passivation coating, and planarization layer. It has a low dielectric constant (3.5 at audio frequencies) and can be processed at temperatures below 450°C. These features make PI attractive to the integrated circuit industry. One disadvantage of this material is that, like most polymers, it is hygroscopic. Moisture can lead to such reliability problems in integrated circuits as increased insulator conductivity, loss of adhesion, and corrosion. It is important to quantify the moisture uptake in polyimide so that the reliability implications of its use can be fully understood. In this study, the steady-state moisture uptake of the model PI pyromellitic dianhydride-oxydianiline (PMDA-ODA) is reported. The moisture uptake is measured using a Cahn 1000 Microbalance with a 1-μg resolution. The samples are prepared by spin-coating one or more layers of the precursor polyamic acid onto 2-in silicon substrates. The moisture uptake in these polymers is found to be linearly related to ambient relative humidity, and the maximum moisture uptake by weight is 3.2%. The moisture uptake in PI is also shown to be a bulk absorption rather than a surface adsorption phenomenon.

INTRODUCTION

Polyimide (PI) is used extensively in the microelectronics industry in a wide variety of applications that include interlayer dielectrics in integrated circuits,[1-4] intermetal insulators in high-density interconnect packaging schemes,[4-6] and thermal–mechanical passivation buffer protection layers.[1-3]

PI has several advantages that make it attractive for microelectronics applications. It has a low dielectric permitivity, (ϵ_r is about 3.2–3.4 at audio frequencies[7]), it is an excellent planarizer,[3,8-10] and is thermally stable up to 400°C.[1,3] Moreover, the driving forces in VLSI technology include the use of dry etching and low-temperature processing. PI can be plasma etched[10] and fully processed at temperatures of 400°C or below. Despite these advantages, there are potential problems associated with PI usage. The foremost of these is that PI absorbs moisture.[7] This hygroscopic behavior can lead to such reliability problems in integrated circuits as increased insulator conductivity, loss of adhesion, and corrosion.[2] On the other hand, PI can be used to implement a solid-state relative humidity (RH) sensor because the dielectric permittivity is linearly related to the ambient RH.[7] In such a sensor, the PI film is used as the dielectric material of a parallel plate capacitor; thus, an increase of RH value will increase the value of the capacitor.[7,11]

In this paper, we characterize the hygroscopic behavior of PI using gravimetric measurements. This measurement technique yields a direct indication of the amount of water absorbed by the PI film. The samples are prepared using standard integrated circuit fabrication techniques, and the measurement is *in situ* and nondestructive. Therefore, the results provide insight into the behavior of PI films as they are used in microelectronic applications. The PI under investigation is exposed to different ambient RH values and the weight change is monitored. We investigate the moisture absorption in PI by varying both the thickness of the PI film and the number of layers of PI coatings on the sample.

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EXPERIMENTAL

Setup

Figure 1 shows a schematic diagram of the gravimetric measurement system. Moisture uptake in the PI samples is measured using a Cahn-1000 microbalance with a resolution of 1 μg. A PI sample is placed inside a customized balance chamber that isolates the sample from the outside ambient RH and temperature. The air inside the balance chamber is controlled by a programmable moisture generator system built by Watlow/Winona Inc. The RH of the sample air is measured using a chilled-mirror hygrometer (General Eastern Model M-1). Both the microbalance and the hygrometer have analog outputs that are connected to two digital voltmeters (DVM). The DVMs have digital I/O (IEEE-488) ports that are connected to a computer. The computer used in this system is an IBM PC/XT compatible, which logs the data from the DVMs and downloads the instructions for the moisture generator to regulate the dewpoint and the temperature of the sample air via the IEEE-488 bus.

The sample chamber in the microbalance has been designed to minimize noise in the measurement. It is made using a double wall tube configuration with an upper ground-glass ball joint to connect it to the weighing unit of the balance. There is an inlet just below the ball joint and an outlet at the bottom of the chamber to allow the sample air to flow through the chamber. The inner wall extends from the ball joint to a quarter of the total length of the tube. The PI sample is hung between the bottom of the inner wall and the bottom of the sample chamber. The inner wall ensures minimal turbulence to the sample. Turbulence causes the sample to oscillate, which will lead to errors in the weight reading. To further reduce the turbulence, the air flow is limited to a maximum of 1.8 L/min. The air flow rate is monitored using a rotameter with a sapphire float.

The supply air for the moisture generator comes from a central air compressor at 90 psi. This compressed air is passed through a 0.3-μm air filter to provide clean air to the moisture generator and its pressure is regulated at 80 psi after the air filter. After the pressure regulator, the air is divided to generate a mixture of dry and wet air. The dry air flow is regulated by a mass flow controller. The wet air stream is generated by passing the filtered air via a mass flow controller through two deionized

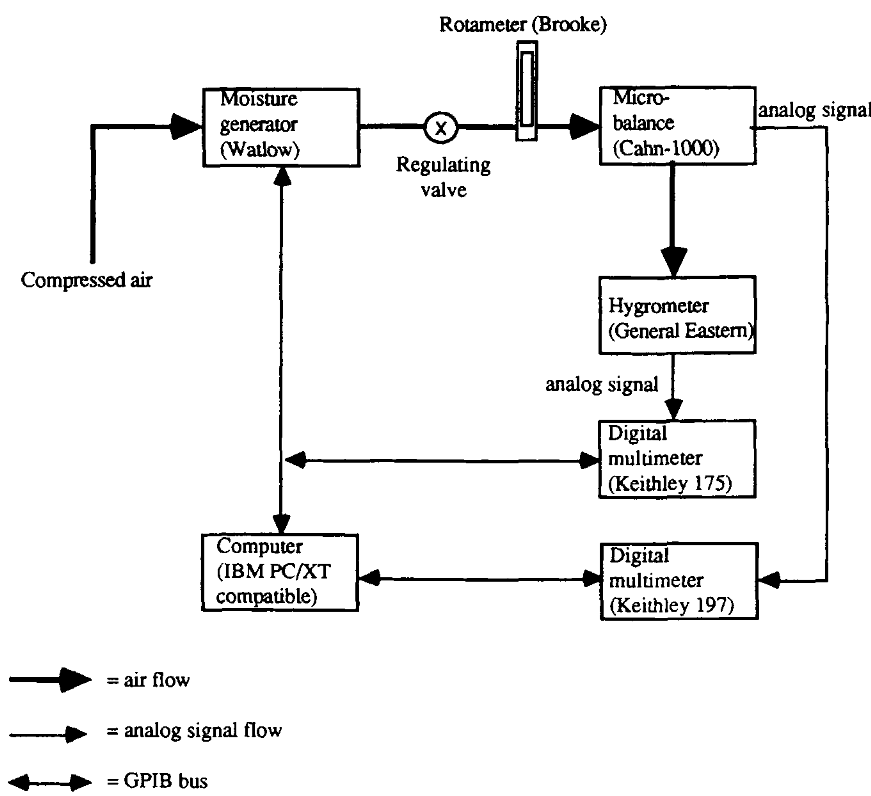

Figure 1 Schematic diagram of the gravimetric measurement system.

water saturator baths to obtain air at 100% RH. A trap is placed after the saturator to prevent any water condensation at the saturator from flowing to the balance. A mixture of wet and dry air is used to achieve a desired RH value. This RH value is repeatable to within ±0.5%. The moisture generator is controlled by a set point programmer (Watlow Model Micro-Pro 2000). The Micro-Pro controls the sample air RH and temperature. The air line, the saturators, and the trap are immersed in a water bath whose temperature can be maintained anywhere between 15 and 95°C.

Sample Preparation

The samples for these experiments are prepared by spin-coating device-grade polyamic acid [pyromellitic dianhydride-oxydianaline (PMDA-ODA)] having 13.6 wt % solids onto polished 2-in silicon wafers. The spin time is 55 sec and the spin speed is varied from 2.1–8.5 kRPM to obtain different film thicknesses between 0.7 and 2.5 μm per layer. These samples are then prebaked at 90°C for 30 min in air to remove the excess solvent. For multiple coats, the samples are prebaked after each application. In this paper, samples with multiple coats of PI will be referred to as multilayer samples. After prebake, samples are cured at 260°C for 6.5 h in air. This long cure time is used to ensure that the film is fully imidized. After cure, the samples were examined with electron spectroscopy for chemical analysis (ESCA) to ensure complete imidization. Our samples are fully imidized based on ESCA analyses reported previously.[12,13]

Procedures

The moisture uptake of a particular sample is determined as follows. The sample is allowed to equilibrate in a dry ambient (4% RH) inside the balance chamber at 23°C. The ambient RH is then rapidly increased and the weight change of the sample is monitored using the data acquisition system described previously. The sample weight is recorded every 2 sec for 15 min. This cycle is repeated at least four times to check the reproducibility of the measurement. Figure 2 shows a typical result for a dry-to-wet transient. It is a plot of mass vs. time for a PI sample (multilayer) exposed to a 4–55% RH change. Note also that the figure shows the trace of four runs carried out using the same conditions. It can be seen from the figure that the reproducibility

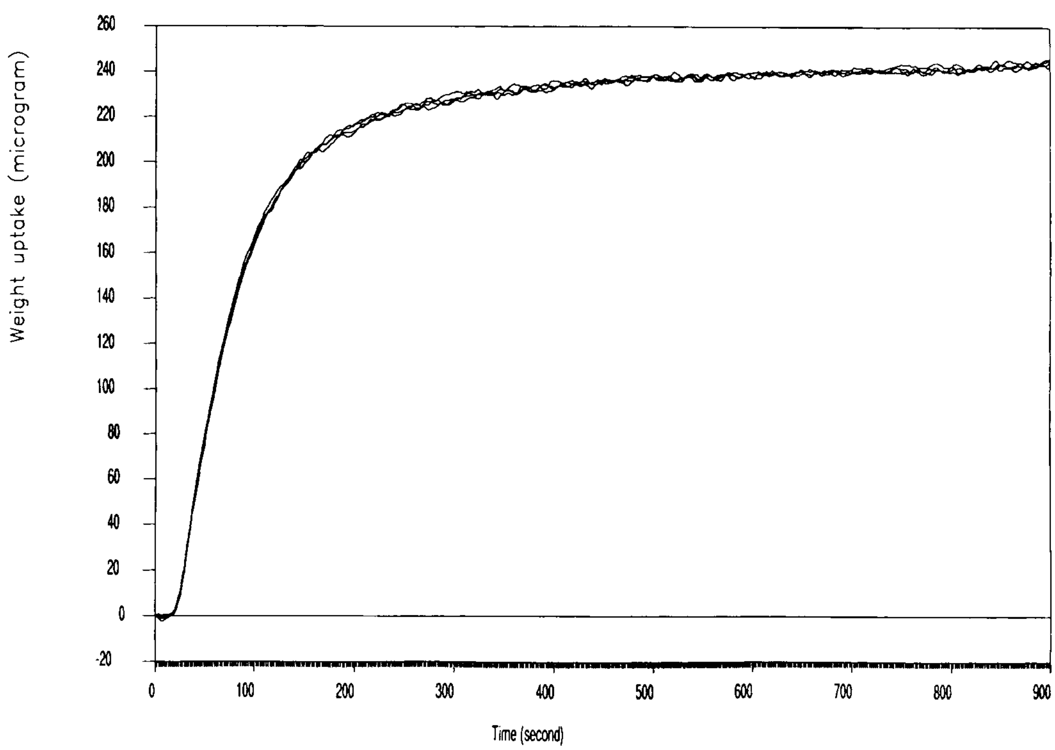

Figure 2 Weight uptake vs. time for a multilayer PI sample exposed to an RH change from 4 to 55% RH. Four different runs are shown to illustrate reproducibility.

Table I Spin Speed Used, Film Thickness, and PI Weight after Cure for Single-Layer Samples

Spin speed (KRPM)	8.1	4.5	2.9	2.1
Thickness (μm)	0.74	1.23	1.78	2.34
Weight (mg)	2.11	3.52	5.09	6.69

in these data is very good. The steady-state moisture uptake in PI as a function of ambient RH is determined by exposing the samples to successively higher RH values ranging from 10–90% RH. Relative humidity values above 90% are avoided to minimize the effects of surface condensation. The diffusion kinetics for moisture in PI have been examined in detail previously.[7,14–16] The moisture uptake was found to be Fickian with a diffusion coefficient of about 5×10^{-9} cm^2/s. This paper will concentrate on the steady-state moisture uptake in PI films.

The weight uptake due to moisture in the PI is determined by averaging the steady-state mass change of four different runs for a given RH swing.

Table II Number of Layers, Film Thickness, and PI Weight after Cure for Multilayer Samples

# of Layers	Thickness (μm)	Weight (mg)
1	1.46	4.29
2	3.49	10.26
3	5.81	17.08
4	8.37	24.60
5	10.52	30.92
6	13.07	38.41

The percent moisture uptake is the ratio of the average weight change due to moisture to the calculated mass of the PI film. The measured weight change accuracy in these experiments is ± 3 μg. The film thickness of the PI sample is measured using a surface profilometer (Tencor Instruments Model Alpha-Step 200) having a resolution of 50 nm. Because the film thickness and the area of the PI film are known, the weight can be calculated assuming a PI density of 1.41 g/cc.[15] Table I shows the spin

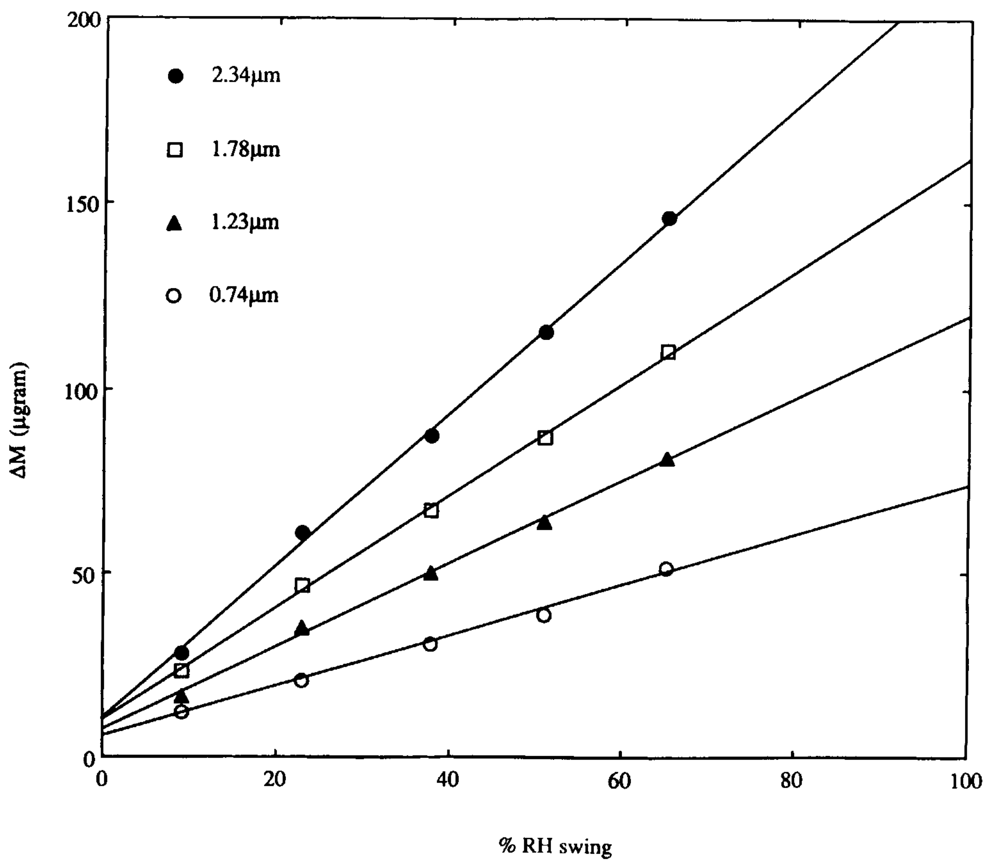

Figure 3 Steady-state moisture uptake vs. RH swing for single-layer samples plotted using PI thickness as a parameter.

speed used and the measured film thicknesses after cure for the single-layer samples and the calculated film weights. Table II provides similar information for the multilayer samples. The number of layers is also indicated in the table.

RESULTS

Figure 3 shows the steady-state weight uptake data for single-layer PI films as a function of RH swing. The RH swing is obtained by subtracting the highest RH value from the lowest RH value for a given run. The low RH value in all cases is about 4%. The family of curves is plotted using the PI thickness (0.74–2.34 μm) as a parameter. It can be seen that the weight uptake is a nearly linear function of RH swing for all film thicknesses. The solid lines represent a least-squares fit to the data; this same fitting method is used for the remaining data presented. Figure 4 shows the steady-state weight uptake as a function of film thickness for single-layer PI films. The family of curves is plotted using the RH swing as a parameter. Note that for higher RH swing, the slope increases. Figure 4 shows that moisture uptake in PI is a bulk phenomenon, i.e., as the film thickness increases, the weight uptake also increases. If we extrapolate these data to the ordinate, there is a nonzero weight uptake for zero film thickness. This may be due to accumulation of water at the Si–PI and/or PI–air film interfaces. This interface phenomenon will be the subject of further study.

Figure 5 shows the steady-state weight uptake data for multilayer PI films as a function of RH swing. The family of curves is plotted using film thickness as a parameter. The number of layers for a given thickness in Figure 5 can be found in Table II. The thickness of the multilayer samples ranges from 1.46–13.07 μm. It can be seen that the weight uptake is a nearly linear function of ambient RH swing, which is consistent with the single-layer data. Figure 6 shows the steady-state weight uptake data for the multilayer samples as a function of film thickness. The family of curves is plotted using the ambient RH swing as a parameter. As in the single-layer case, the higher the RH swing, the greater the

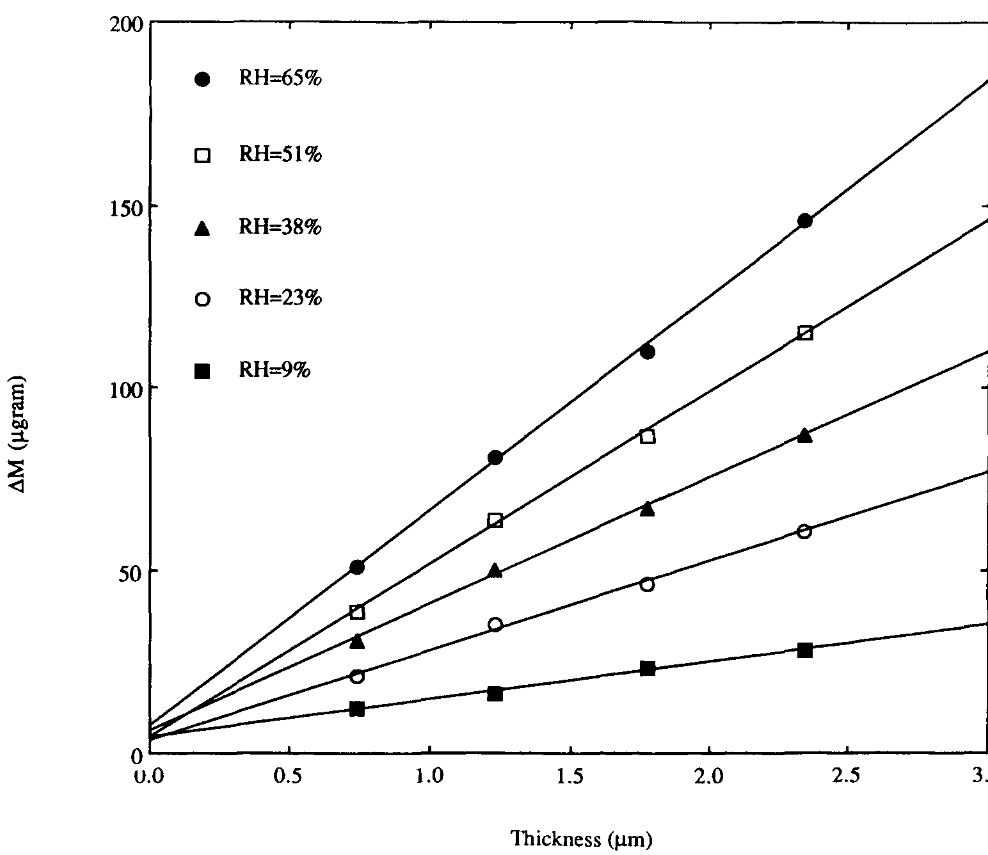

Figure 4 Steady-state moisture uptake vs. PI thickness for single-layer samples plotted using RH swing as a parameter.

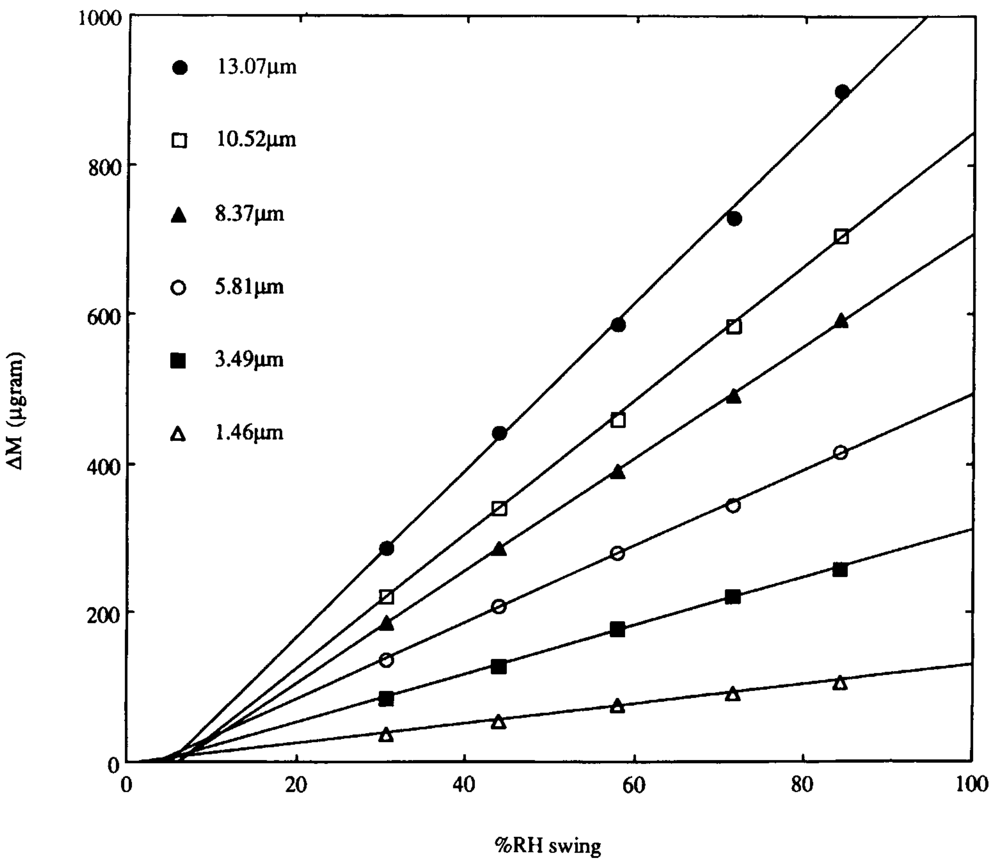

Figure 5 Steady-state moisture uptake vs. RH swing for multilayer samples plotted using PI thickness as a parameter.

slope. This plot again confirms that the moisture uptake in PI is a bulk phenomenon.

The percentage moisture uptake data for the single layer films at 51% RH swing are given in Table III. Note that this value (1.7–1.8%) is nearly independent of film thickness. The percentage moisture uptake for all RH swings is provided in Table IV for the 2.34-μm thick sample, which is representative of the results for all single-layer films. The extrapolated moisture uptake at 100% RH swing for single-layer films is 3.2% by weight.

The percentage moisture uptake data for the multilayer films at 55% RH swing are given in Table V. As before, this value (1.5–1.7%) is nearly independent of film thickness. The percentage moisture uptake for all RH swings is provided in Table VI for the 8.37-μm sample, which is representative of all the results for all multilayer films. The data of Table VI are plotted in Figure 7. The figure shows that the moisture uptake by weight in the multilayer samples is a nearly linear function of ambient RH swing. Extrapolation to 100% RH swing yields a value of 3.0% moisture uptake by weight. This is comparable to the value for single-layer PI films.

DISCUSSION

It has been demonstrated that the moisture uptake in PI is linearly related to the ambient RH at room temperature. Both single- and multilayer films exhibit this behavior. The steady-state room temperature moisture uptake values reported here are comparable to those reported by others. Kliem et al.[18] reported a maximum weight uptake of 2.2% by weight for an unspecified PI; cure conditions and sample preparation were not reported. Samuelson[19] reported a maximum weight uptake of 4.2% for DuPont PSH61453 with unspecified cure schedule. Sacher and Susko[20] reported 4.5% weight uptake for a 127-μm thick freestanding DuPont Kapton film. Malladi et al.[21] reported the weight uptake of an Upjohn #2080 PI as 0.046 g H_2O/cm^3. The Upjohn films were spin-cast on a quartz substrate, the solvent was evaporated at 90°C for 30 min, and the films were not cured. The range of the reported values for moisture uptake by weight is about 2–5%. These workers did not, in most cases, report moisture uptake over a range of RH values. In addition, as can be seen from this summary, the polymer

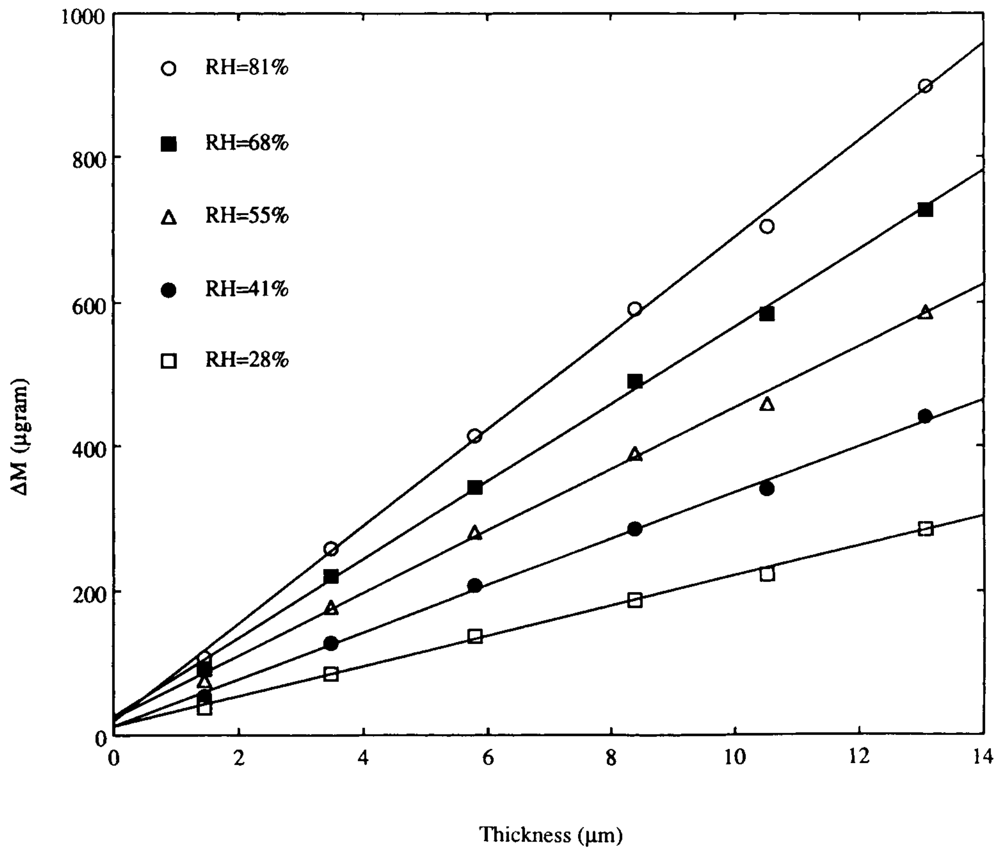

Figure 6 Steady-state moisture uptake vs. PI thickness for multilayer samples plotted using RH swing as a parameter.

chemistries were not reported. Furthermore, the cure conditions and handling procedures are not provided. In some cases, the PI samples are not fully cured. We have shown in previous work[22] that maximum moisture uptake is a strong function of cure schedule used.

In the present study, polymer chemistry, cure schedule, and handling procedures are carefully documented. The results presented here therefore serve as a baseline study for the model PMDA-ODA chemistry. Several outstanding issues remain to be addressed regarding the reliability implications of the use of PMDA-ODA films in integrated circuits. In particular, the steady-state moisture uptake and diffusion kinetics of moisture in PI must be examined as a function of processing parameters and environmental aging. These studies are currently un-

Table III PI Thicknesses and Percentage Moisture Uptake by Weight for Single-Layer Samples Exposed to an RH Change from 4–55% RH

Thickness (μm)	0.74	1.23	1.78	2.34
%ΔM	1.8	1.8	1.7	1.7

Table IV Percentage Moisture Uptake by Weight for a Range of RH Swings for a Single-Layer 2.34-μm Thick PI Film

RH swing (%)	9	23	38	51	65
%ΔM	0.4	0.9	1.3	1.7	2.2

Table V PI Thicknesses and Percentage Moisture Uptake by Weight for Multilayer PI Films Exposed to an RH Change from 5–59% RH

Thickness (μm)	1.46	3.49	5.81	8.37	10.52	13.07
%ΔM	1.7	1.7	1.6	1.6	1.5	1.5

Table VI Percentage Moisture Uptake by Weight for a Range of RH Swings for an 8.37-μm Thick Multilayer PI Film

RH swing (%)	28	41	55	69	81
%ΔM	0.8	1.2	1.6	2.0	2.4

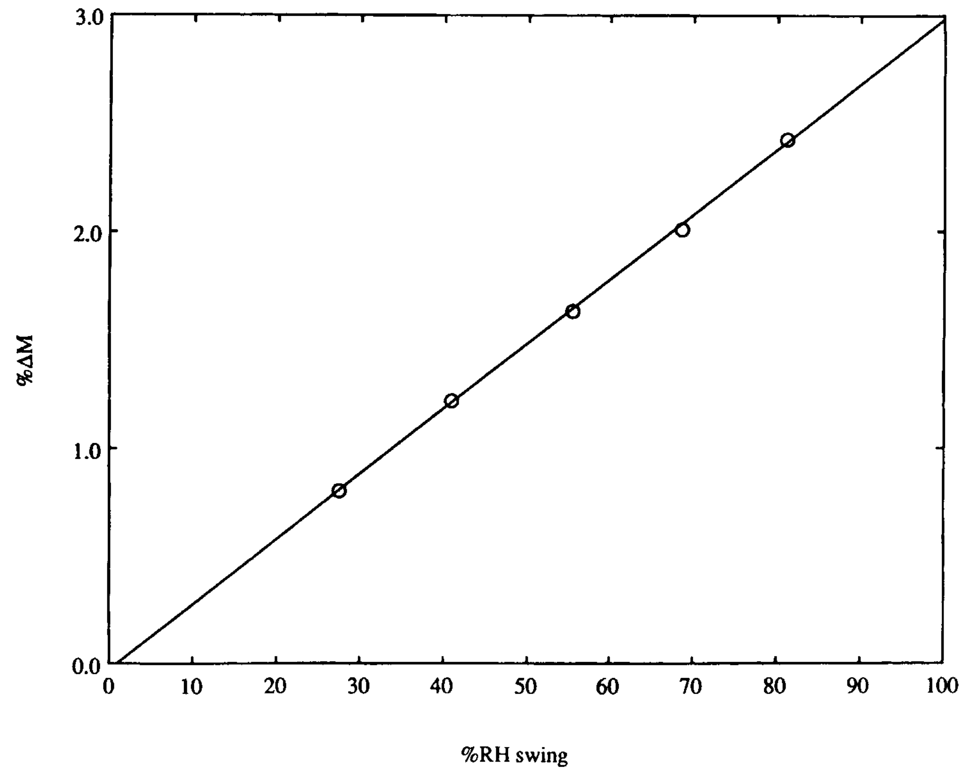

Figure 7 Percentage moisture uptake by weight vs. RH swing for a multilayer sample having a PI thickness of 8.37 μm.

derway in our laboratory and the results presented here will facilitate the interpretation of subsequent experimental work.

CONCLUSION

We have shown that moisture uptake in PI is a bulk phenomenon regardless of the number of layers of film. The weight uptake of moisture in PI is a nearly linear function of both film thickness and ambient RH at room temperature. The extrapolated bulk moisture uptake in PI films for a 100% RH swing is approximately 3% by weight. The steady-state moisture uptake in PI is nearly identical for single- and multilayer films. Since the film samples were prepared using standard microelectronic fabrication technique and the measurements were *in situ* and nondestructive, the results presented here reflect the behavior of the PI films in an integrated circuit environment.

Because the chemistry and processing details are provided here, the experimental results presented provide baseline data for comparison purposes. The water absorbed by PI may lead to reliability problems in microelectronic applications. In particular, preliminary studies in our laboratory indicate that long-term exposure to high temperature and humidity environments leads to increased moisture uptake in PI and changes in its dielectric properties. Results of this work will be reported subsequently.

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