Sensors and Actuators B, 13–14 (1993) 432–436

Measurement of relative adhesion and surface properties of polyimide films using a surface acoustic wave sensor

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Abstract

A surface acoustic wave (SAW) sensor is used to study the relative-humidity response of thin polyimide films on quartz, where interfacial and surface properties are varied. The results show differences in the comparative SAW humidity response for films applied with and without adhesion promoter and with and without a chromium interface layer deposited between the substrate and the polyimide film after temperature and humidity aging. Polyimide films were examined that were both sputter cleaned and non-sputter cleaned. The humidity response is particularly sensitive to the surface treatment of the polyimide film. A theoretical analysis has been done to obtain information on the physical mechanisms responsible for the SAW sensor humidity response. The analysis identifies three primary film properties that can influence this response. These properties are changes in density, elastic constants and stress of the film as a function of humidity. The more dominant of these factors appear to be density and elastic-constant changes.

1. Introduction

Polyimide (PI) films are of high interest due to their widespread use as an insulator in microelectronic devices. Film reliability and how it can be affected by film surface properties and adhesion are particularly important. Surface properties can be affected by the processing steps used during device fabrication, while adhesion can be affected by the characteristics of the film–substrate interface and temperature and humidity (T&H) aging. The relationship between the SAW humidity response and the relative adhesion strength of PI films on quartz substrates is of great interest, since it could have application as a nondestructive indicator of adhesion strength. Previous work has shown that there is a relationship between the humidity response, adhesion and surface properties [1, 2]. The current work shows how this response is affected by T&H aging and also shows the effect of interface characteristics on film removal. A comparison of the results from perturbation and exact numerical theory for a coated SAW device is made in order to determine whether the perturbation approximation can be used for PI layers. The predicted SAW phase change as a function of humidity is then compared to the experimental results.

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2. Theory

Wohltjen [3] used an expression derived from perturbation theory which gives the change in the SAW velocity of a SAW device as a function of the overlay parameters. This expression includes the mechanical effects introduced by a thin, non-viscous, insulating, isotropic overlay on an isotropic substrate. The equation for the change in SAW velocity is as follows:

$$\frac{\Delta V_R}{V_R} = (k_1 + k_2) f h \rho' - k_2 f h \left[\frac{4\mu'}{V_R^2} \left(\frac{\lambda' + \mu'}{\lambda' + 2\mu'} \right) \right] \tag{1}$$

V_R is the Rayleigh wave (SAW) velocity (m/s) for a bare substrate, ΔV_R is the change in SAW velocity due to the layer, h is the film thickness (m), ρ' is the film density (kg/m^3), λ' and μ' are the film Lamé constants (N/m^2), f is the SAW frequency and k_1 and k_2 are frequency-dependent substrate material parameters. The last term on the right-hand side of eqn. (1), which is a function of the Lamé constants, λ' and μ', can be ignored for soft polymers ($4\mu'/V_R^2$ less than 100), but is significant for PI where $4\mu'/V_R^2$ is much greater than 100.

0925-4005/93/$6.00

TABLE 1. Phase changes predicted by the numerical solution vs. perturbation theory for a 1.2 μm PI film at 75% RH

	Phase change (degrees) due to			Approx. total	Exact total
	Density	Elastic constants	Stress		
Exact	−28.0	−18.0	−2.4	−48.4	−47.7
Perturbation	−19.4	−7.2	0.0	−26.6	−26.6

Computer software has been developed at the University of Maine [4] that calculates numerically, exact phase (Φ) and velocity (V) information for SAW propagation in a layered piezoelectric substrate where the change in phase ($\Delta\Phi$) and change in velocity (ΔV) are related by $\Delta\Phi/\Phi = -\Delta V/V$. This program has been modified to include the effect of film-induced stress on the substrate [5]. Since relative-humidity variations affect the PI film parameters, such as density, elastic constants and stress, the theory can be used to predict the change in SAW phase as a function of relative humidity (RH) [6]. In order to understand the nature of the interaction between humidity and the PI-SAW sensor, it is important to know the approximate contribution of each film parameter to the total change in SAW phase. Table 1 gives the approximate relative contributions to SAW phase change from the change in one film parameter as a function of RH while the other parameters are held constant, from the numerical solution. The exact total from the numerical solution is also given along with the values from perturbation theory for a 1.2 μm PI film at 75% RH. As can be seen, the perturbation solution provides some indication of the relative contributions from density and elastic constant changes, but the magnitudes are not comparable to the numerical solution for this case.

3. Experimental

The PI studied is PMDA-ODA manufactured by Du Pont. The polyamic acid was spin coated onto the entire SAW sensor and then patterned using standard integrated-circuit fabrication techniques. It had a final thickness after curing of approximately 1.2 μm. A typical sensor configuration is shown in Fig. 1. In this example one channel has a polyimide film with adhesion promoter on the propagation path, while the second channel has a polyimide film without promoter. The adhesion promoter used was OVSC's A-1100. Some of the film samples also had a 300 Å thick chromium interface layer. The electronic set-up and the environment control system are similar to those described in ref. 1.

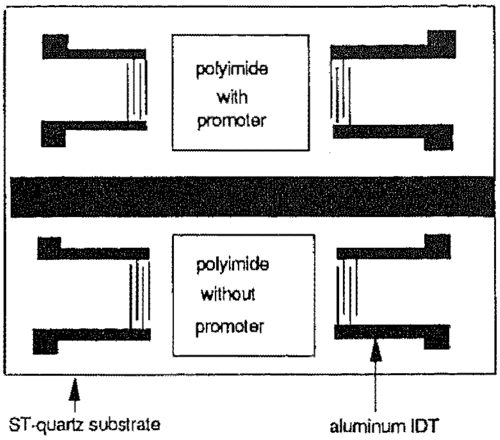

Fig. 1. The SAW adhesion sensor with PI films.

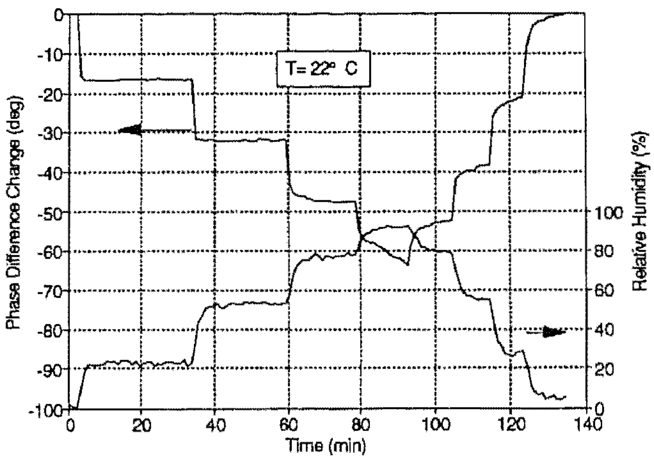

Fig. 2. The SAW sensor humidity response for an unsputtered 1.2 μm thick polyimide film.

4. Results and analysis

4.1. Humidity response

A typical PI-SAW sensor humidity response for a cured PI sample is shown in Fig. 2. The humidity in the test chamber is controlled by calibrated rotameters and was brought from 0 to 100% RH in 25% RH increments in order to assess the linearity of the response. The lower curve is referenced to the right-hand y-axis and is the humidity in the chamber as recorded by the Omega humidity sensor. The upper curve is the response of the PI-SAW sensor and is referenced to the left-hand y-axis. It can be seen from the large response that the PI film readily absorbs moisture and that the response of the PI-SAW sensor to humidity changes is quicker and more uniform than the response of the Omega sensor. The negative phase-difference change directly corresponds to a slowing of the SAW velocity (loading) and is due to water being absorbed by the film. Figure 3 shows the PI–SAW sensor response for a sputter-cleaned film. As can be

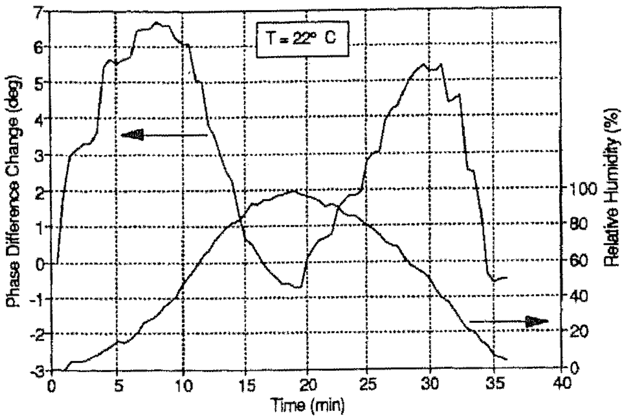

Fig. 3. The SAW sensor humidity response for a sputtered 1.2 μm thick polyimide film.

TABLE 2. The change in phase as a function of changes in density, elastic constants and stress of the layer for a 1.2 μm polyimide film from the exact solution compared to experimental results

% RH	Phase change from	
	Exact theory	Experiment
0	0	0
25	−16.0	−16.0
50	−32.2	−32.0
75	−47.7	−47.0
100	−63.1	−63.0

seen, the response is much smaller and in the positive direction, indicating that little water, if any, is being absorbed into the film. The sputter cleaning has apparently altered the surface chemistry of the film, changing it from hydrophilic to hydrophobic. Treatment with potassium hydroxide has been shown to reverse this effect [2].

Table 2 shows the theoretical SAW phase change calculated from the exact theory as a function of humidity, compared to the phase change from Fig. 2. The theoretical value, which includes the effect on phase caused by humidity variations in film density, elastic constants and stress, compares well with the experimental results for a 1.2 μm thick PI film cured at 400 °C. Both theoretical and experimental results change linearly with changes in relative humidity. The dominant mechanisms for the SAW humidity response appear to be changes in density and elastic constants, while changes in film stress account for about 10% of the response.

4.2. *Effect of T&H aging on the difference response*

Rothman [7] has shown that when a PI film on SiO_2 is exposed to long periods of high temperature and humidity (T&H), the adhesion weakens for the film without adhesion promoter. In order to verify this phenomenon and see whether the SAW sensor can detect adhesion weakening, several PI films were exposed to 100% RH at 85 °C for several hours.

The phase difference response for two KOH-treated films, one with promoter and one without, before T&H treatment is shown in Fig. 4. When compared to the response after T&H in Fig. 5, a 50% increase in the response magnitude at the 25, 50 and 75% RH steps is observed. This result indicates that the film without promoter has an increased humidity response relative to the film with promoter after T&H treatment. It has been proposed that a larger humidity response may indicate weaker adhesion [2]. This may be due to additional water penetrating the film–substrate interface where there is weaker adhesion.

It should be noted that the humidity response becomes erratic for humidity levels of over 75%. This erratic response is due to the fact that as water is absorbed into the film the SAW signal attenuates. When the

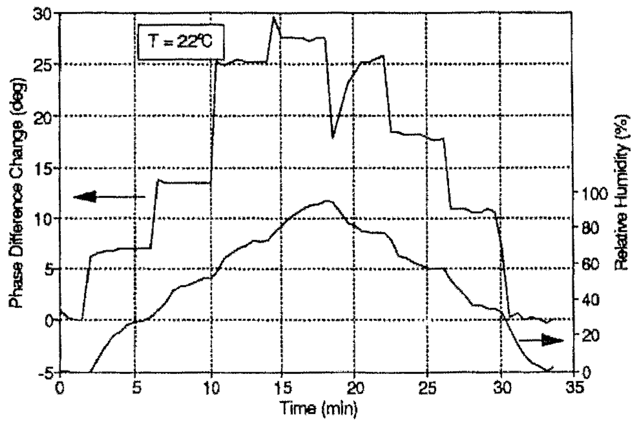

Fig. 4. The SAW sensor humidity difference response for a sputtered polyimide film with promoter referenced to a sputtered film without promoter.

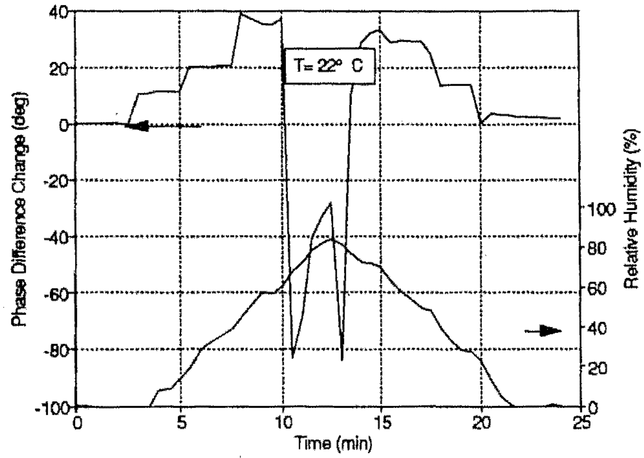

Fig. 5. The SAW sensor humidity difference response for sputtered polyimide films after T&H aging.

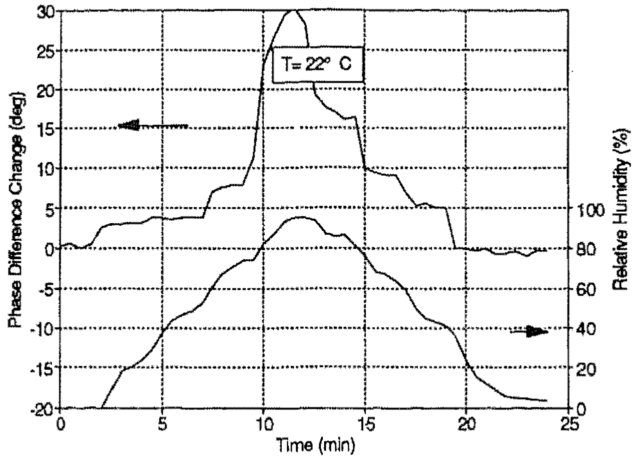

Fig. 6. The SAW sensor humidity difference response for an unsputtered PI film on chromium referenced to a unsputtered PI film on quartz before T&H aging.

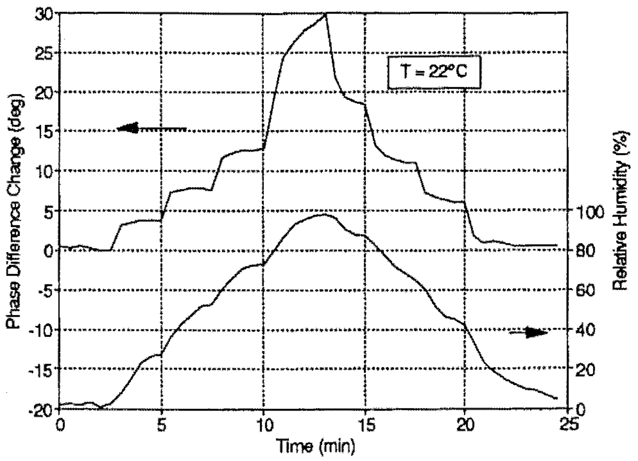

Fig. 7. The SAW sensor humidity difference response for an unsputtered PI film on chromium referenced to an unsputtered PI film on quartz after T&H aging.

SAW signal attenuates to the level of the sensor background noise, changes in the phase of the SAW are no longer detectable. Only films that absorb large amounts of water appear to be subject to this effect.

T&H treatment of 100% RH for several days was also given to PI films with and without a chromium interface. It has been demonstrated by others [8] that chromium can improve the adhesion of PI films. The results for PI films with and without chromium were similar to the results for PI films with and without promoter. Figure 6 shows the difference response before T&H aging, while Fig. 7 shows a larger response after T&H aging for the 50 and 75% RH steps.

4.3. Film removal

Studies of PI film removal were conducted while the SAW sensor response was being observed. The film on one channel was slowly scraped off in strips perpendicular to the SAW propagation direction. One quarter of the film was removed at a time by this method. The experiment was conducted on several films, all with different interface or film characteristics at 22 °C and 25% RH.

TABLE 3. Phase change resulting from the loading effect of a 1.2 μm PI film

Film configuration	Phase change (deg.)
Theory	−940
Cured with promoter	−940
Cured no promoter	−935
Cured 10% promoter	−960
Uncured	−103

The results for cured PI films approximately 1.2 μm thick without and with promoter after T&H treatment are shown in Table 3. The total response for film with promoter is only one or two percent larger than the response for film without promoter. This indicates that the effect of the adhesion promoter on the overall loading effect of the PI film to the SAW sensor is not measurable even after T&H treatment. The results of a removal test on PI film approximately 1.2 μm thick prepared with 90% adhesion depromoter and 10% promoter are also given. The total response magnitude is similar to that of the other films. The theoretical value for phase shift is also given in Table 3 and shows excellent agreement with experiment for the cured film.

A removal test was also conducted on an uncured film approximately 1.8 μm thick. The total phase shift was much less for the uncured film than the cured film. Since the uncured film has similar or greater mass than the cured films and is much softer, it was expected to have a loading effect on the SAW sensor similar or greater than that of the cured film. However, this is not what was observed. Since the material properties are not available for uncured PI, an exact theoretical prediction of phase change cannot be made. One possible explanation for the small phase change is the poor adhesive bond between the film and substrate prior to curing. This poor bonding may also explain why the RH response of uncured film is also small [1]. A second possible explanation is that a weakening of the adhesive bond may have occurred during a storage period of approximately two years.

5. Conclusions

Exact numerical theory shows that changes in PI film density, elasticity and stress all make significant contributions to the SAW humidity response. Comparisons of perturbation theory with exact theory show significant differences in the predicted phase change for PI films 1.2 μm thick. SAW sensor humidity-response comparisons of PI films with different interfaces demonstrate that it may be possible to measure relative adhesion strengths for these films. All PI films with better nominal adhesion, due to adhesion promoter or a chromium interface, exhibited a smaller SAW humidity response than films with no adhesion enhancement. Aging the PI films under high temperature and humidity increased the SAW humidity response. This is most likely due to weakening of the adhesion. A model that relates the humidity response to adhesion and weakening adhesion is proposed. Namely, water more easily penetrates an interface bonded through dipole–dipole interactions (no promoter) than one bonded by acid–base bonds (with promoter). In addition, the SAW sensor can detect differences in the surface treatment of PI films. The primary advantages of the SAW sensor in adhesion studies are that it is a nondestructive method of measuring relative adhesion strengths and that it has the potential to be used *in situ* with test samples. The SAW sensor's high sensitivity to the effects of changes in surface chemistry of polyimide films also suggests its use as an *in situ* process-control monitor for microelectronic device fabrication.

Acknowledgements

This work was supported in part by an SUR grant from the IBM Corporation and the ISHM Educational Foundation. Thanks are also due to J. Andle for the use of his Layers program and R. Falconer and W. Unertl for many helpful discussions.

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Biographies

David W. Galipeau received his BS degree in electrical engineering from the University of Rhode Island in 1971. He then worked for AT&T in technical operations and planning at a Bell operating company from 1971 and 1987. He received his Ph.D. degree in electrical engineering in 1992 from the University of Maine. He joined South Dakota State University as an assistant professor of electrical engineering in August, 1992. His major research interests include microsensors, electronic materials and ultrasonic thin-film characterization techniques.

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