Mechanical and Piezoresistive Properties of Graphite-Filled Polyimide for Hybrid Micromachined Systems

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Abstract

Graphite/polyimide composites are characterized for the material properties relevant to hybrid micromachined system applications. The characteristics of interest at this time include the general mechanical properties of the thin film, residual stress and plane strain modulus, as well as the electromechanical property, piezoresistivity. The characteristics of interest are evaluated for composite films with a graphite loading range of approximately 15 to 25 percent using an in situ method of evaluation involving load/deflection/resistance measurements. The results show that the residual stress remains constant and the plane strain modulus rises with increasing graphite loading. An 18% graphite loading yielded the maximum piezoresistive coefficient of 16.8%.

Key Words: Piezoresistive, Polyimide, Plane strain modulus, and Residual stress

Introduction

The advantages of polyimide films for use in microelectronics related applications has been well documented. Polyimides have proven useful in hybrid microelectronic technology as both a multilayer interconnect dielectric and multichip module material due to their superior insulating properties and low relative permittivity. Polyimides are also used extensively as planarization materials in the fabrication of integrated circuits. Conductive metal-filled polyimides have been widely studied for applications including die attach, thermistors, electromagnetic shielding, anti-static devices, pressure and chemical sensors as well as aerospace applications where both a cost and weight savings can be realized over conventional metallic components. A large number of conductive fillers have been characterized for these applications including predominantly metallic fillers such as salts of silver, gold, palladium, cobalt, lanthanide and copper [e.g. 1-6]. Although these conductive materials exhibited interesting and useful characteristics, the majority were not compatible with conventional methods of microelectronics processing (e.g. plasma etching for pattern definition) needed for micromachined device fabrication. Studies have also been performed to characterize organic fillers including graphite, but for applications other than micromachined systems.

The purpose of our research is to characterize graphite/polyimide thin film composites for the material properties relevant to microsensor and actuator systems applications. The characteristics of interest at this time include the general mechanical properties of the thin film, residual stress and the plane strain modulus, as well as the electromechanical property, piezoresistivity. Many techniques have been demonstrated for measuring the mechanical properties of thin films. These techniques include the common substrate curvature technique as well as many others which utilize micromachining technology. Those utilizing micromachining techniques and devices include stationary and movable structures [7-12], and load/deflection testing of cantilever beams [13-15] and membranes [16-20]. Load/deflection of membranes has the advantages of (1) simultaneous measurement of the residual stress and the plane strain modulus and (2) being independent of the materials index of refraction and (3) being relatively insensitive to the surface roughness. The second and third advantages are essential for the characterization of the graphite/polyimide composite due to the physical nature of the suspended composite material. In the following sections, the material properties are determined using an *in situ* membrane load/deflection technique involving

simultaneous measurement of load, deflection, and resistance. The material properties of the composite films are evaluated for a graphite loading range of 15 to 25 percent.

Experimental

The graphite/polyimide material is composed of submicron graphite particles obtained from Johnson Matthey Electronics and DuPont PI-2555 polymide (a BTDA/ODA-MPDA formulation). The composite is formed by introducing various weight percentages (loadings) of the graphite particles into the polyimide. The materials are mixed using a ball mill rotating at 4-5 rpm for a period of at least 72 hours to insure homogeneity of the mixed composite solution. The composition of the films are based upon the weight percentages of the two constituents in the cured film. The weight of the polyimide is calculated using the average percent solids of the polyimide solution.

To characterize the composite material, load/deflection test are performed using long rectangular membranes of the thin films (thickness: 12 - 15 µm) which are fabricated on silicon substrates. The suspended membranes of the graphite-filled polyimide are realized using micromachining techniques. In the fabrication process, two inch <100> silicon wafers are anisotropically etched in a 20 wt% potassium hydroxide solution heated to 56°C using SiO_2 as an etch mask [21], Figure 1a. A 3 - 5 µm thick, heavily boron doped ($>10^{20}$ / cm^3) layer is used as an etch stop layer [16] on the polished side to produce a silicon membrane, Figure 1b. After the silicon etch is complete the silicon dioxide is removed, followed by deposition of an insulating layer of PECVD Si_3N_4. The Si_3N_4 isolates the overlying composite material from the underlying heavily doped p^+ boron region. A thin film of composite material is applied over the Si_3N_4 using a multicoat procedure, Figure 1c. A single coat of the multicoat procedure consists of a 3000 rpm, 30 second spin cycle followed by a 15 minute soft bake at 150 °C. The multicoat film is then fully cured at 400 °C for 1.0 hours in a conventional oven. The p^+ etch stop layer and Si_3N_4 thin films are removed from the membrane regions by exposing the unpolished side of the wafer to a 95% CF_4 / 5% O_2 plasma, resulting in the finished composite membrane. At this point, the mechanical properties (Young's modulus and residual stress) can be determined from the load/deflection behavior of the membrane.

In order to determine the piezoresistive coefficient, the fabrication process for the membranes must be extended to patterning the film and depositing electrodes for resistance measurements. The film is patterned into a 32 mm wide strip using a 100 % O_2 plasma and sputtered aluminum as the etch mask. The electrodes are then patterned in the aluminum etch mask as the final step in the membrane fabrication process, Figure 1d.

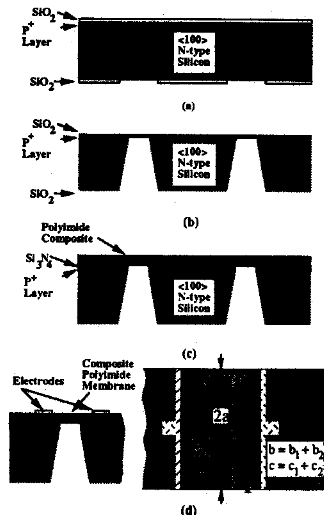

Figure 1. Fabrication process for the rectangular membranes of composite material. The membranes are used to determine the material characteristics by load/deflection techniques.

The characterization of the thin films is carried out using a material characterization station which allows tight control of the load applied to the membrane. The station operates by using dual vacuum lines. Vacuum 1 is used to seal an adaptor

plate (plate depends on the membrane size to be tested) to the base plate of the characterization station as well as to seal the membrane sample to the surface of the adaptor plate. Vacuum 2 is controllable and acts as the load to the membrane region. A pressure transducer is used to monitor the amount of the load induced by vacuum 2. The induced deflection at the center of the membrane is measured using a z-axis digimatic indicator. As the membrane is deflected, the resistance is monitored by attaching probes to the electrodes patterned on the composite material.

Mechanical Properties

In this work, the mechanical characteristics are determined by an analysis of the load/deflection behavior of a membrane using an energy minimization approach [22], but modified to account for the presence of residual tensile stress [16-20] and rectangular dimensions. This theory leads to the following relationship between applied pressure and lateral deflection:

$$\frac{P a^2}{d t} = 2\sigma_0 + \frac{4E}{3(1-\nu^2)}\left(\frac{d}{a}\right)^2 \qquad (1)$$

where P is the applied pressure, E is the Young's modulus of the film, σ_0 is the residual stress in the film, ν is Poisson's ratio of the film, 2a is the membrane width, t is the film thickness, and d is the membrane deflection at its center. By plotting load/deflection data in accordance with equation (1), the residual stress can be extracted from the y-intercept and plane strain modulus ($E / (1-\nu^2)$) can be extracted from the slope. Typical load/deflection characteristics are shown in Figure 2.

The mechanical characteristics can be obtained by fitting the data to equation 1, as shown in Figure 3. The scatter at low values of deflection in Figure 3 is due to the difficulty in measuring small deflections using our material characterization station.

The experimentally determined residual stress and plane strain modulus for a variety of film loadings are shown in Table I. The data represents the average values obtained from load/deflection test performed on three membranes from each graphite loading percentage. The error is given as the standard deviation of the three samples. Load/deflection tests were performed at 26 °C with a relative humidity of 35%. As can be seen in Table I, the residual stress of the thin film is not significantly affected by the percentage of graphite

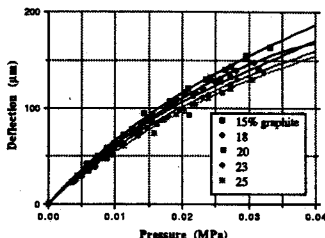

Figure 2. Typical load/deflection characteristics for the graphite/polyimide composite material. The membrane was 30 mm long, 5 mm wide, and had a thickness range of 12 to 15 µm.

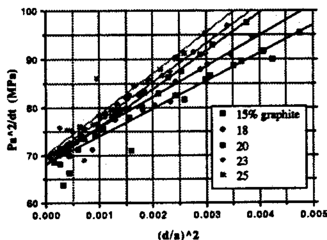

Figure 3. Load/deflection data plotted in accordance with equation 1 for the graphite/polyimide composite films. The residual stress can be determined from the y-intercept and the plane strain modulus from the slope.

loading for the range of interest, 15% to 25%. This result indicates that the BTDA-ODA/MPDA dominates the residual stress characteristic. However, the plane strain modulus of the films does

Table I. Experimentally determined residual stress and plane strain modulus for the composite material. The graphite loading range of the composite is 15% - 25%.

% Graphite	Residual Stress (MPa)	Plane Strain Modulus (MPa)
15	35.0 ± 0.2	4.1 ± 0.4
18	35.2 ± 0.4	4.9 ± 0.3
20	33.9 ± 0.3	5.4 ± 0.4
23	34.6 ± 1.2	6.3 ± 0.6
25	34.9 ± 0.7	6.7 ± 0.4

show a dependence on the amount of graphite loading. As the amount of graphite increases in the composite, the plane strain modulus of the material also increases. This result is expected based on the fact that the graphite particles characteristically have a much higher Young's modulus than the polymer.

Piezoresistive Coefficient

The piezoresistive characteristics are determined by similar load/deflection techniques in which the resistance across the membrane is monitored as a function of deflection. Using the experimentally determined resistance/deflection relationship, coupled with the model presented below, the piezoresistive coefficient can be obtained. It is assumed that the resistivity of the composite material has the form:

$$\rho = \rho_0(1 + \lambda\,\varepsilon) \tag{2}$$

where ρ_0 is the resistivity of the unstrained composite material, λ is a dimensionless piezoresistive coefficient, and ε is the strain induced by the deflection. The total resistance of the material between the electrodes can be modeled as a combination of series and parallel resistors. Using this model, the total resistance as a function of deflection has the form:

$$R(d) = \rho_0\left(\frac{\alpha_1 + \alpha_2\lambda\, d^2}{\alpha_3 + \alpha_4\lambda\, d^2}\right) \tag{3}$$

where:
$\alpha_1 = (2a + c)^2$
$\alpha_2 = 4\,(2a + c) / 3a$
$\alpha_3 = L\,t\,(2a + c) + c\,b\,t + 2\,a\,b\,t$
$\alpha_4 = 4\,b\,t / 3\,a$

Therefore, the α's are constants dependent on the dimensions of the membrane and the electrode length and spacing, defined in Figure 1d. Using this model for R(d), the piezoresistive coefficient (λ) can be determined from the slope of an appropriate plot of equation (3), $[\alpha_1\rho_0 + \alpha_3 R_d]$ versus $[(\alpha_2\rho_0 + \alpha_4 R_d)\, d^2]$.

Characterization of the piezoresistive coefficient is perhaps the most interesting property of the material with respect to micromachining applications. A typical resistance/deflection curve is shown in Figure 4. The curve illustrates the quadratic dependence of the resistance on the deflection (as predicted by equation 3). From this data, the piezoelectric coefficient as defined in equation (2) can be determined.

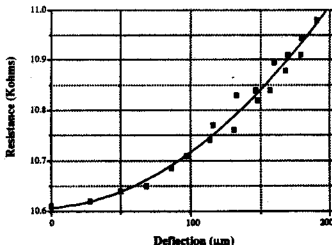

Figure 4. Typical experimental data for the resistance change when applying a load to the membrane, showing the quadratic dependence of the resistance on the deflection.

The final results obtained for the composite film for a graphite loading range of 15 - 25% is shown in Figure 5. As can be seen, the maximum

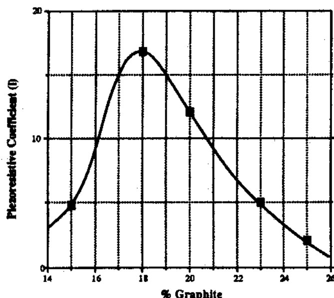

Figure 5. Piezoresistive coefficient of the graphite/polyimide composite material. The maximum piezoresistive coefficient is obtained for a loading of 18% graphite and tails off for loading percentages above and below the 18% value.

piezoresistive coefficient is obtained for a graphite loading of 18%. The obtained piezoresistive coefficients are quite large. For example, selecting a typical strain of 1% in a composite thin film with 18% graphite loading will induce a 16.8% change in total resistivity.

The composite is believed to exhibit the piezoresistive effect based upon the fact that conductive graphite particles are suspended in an insulating polyimide material and the proximity of the conductive particles to one another can be varied by inducing a strain on the material. The action of varying the proximity of the conductive particles results in fluctuations in the resistivity of the strained film.

The piezoresistive coefficient tails off for loading percentages above and below the optimum value as the material becomes increasingly insulative or conductive. This can once again be correlated to the change in proximity of neighboring conductive particles. In loading percentages below the optimum value, the proximity of neighboring conductive particles becomes increasingly larger. Therefore, the change in proximity as a result of induced strain on the material is small resulting in small changes in the resistivity of the film. For loading percentages greater than the optimum value, the number of nearest neighbors increases to the point where the proximity is uneffected by the strain on the material.

Conclusion

A new plasma processable composite material has been introduced for use in microsensor applications. A model has been presented for the determination of the mechanical and piezoresistive characteristics for the thin films of material with residual tensile stress. Using the model, graphite-filled polyimide thin films have been characterized for a range of 15 - 25% using load/deflection techniques. The results indicate that the residual stress is uneffected by variations in graphite loading, while the Young's modulus increases with increased loading. The piezoresistive coefficient has been found to be a maximum at 18% graphite loading. Using the characteristics obtained, microsensor or actuator designs utilizing the piezoresistive property of the graphite-filled polyimide composite can be optimized.

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