High Sensitivity Technique for Measurement of Thin Film Out-of-Plane Expansion

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An absolute, high sensitivity technique for the measurement of the out-of-plane expansion of thin films is presented. To demonstrate the ability of the technique to produce correct results for the thermal expansion of materials, measurements were performed on <0001> single crystal sapphire. A thin polymeric film designed for use as an interlayer dielectric (ILD) was measured to show the utility of the technique to resolve the measurement of displacement in thin films. Additionally, the ability of the technique to measure swelling (or hygrothermal expansion) was demonstrated on a typical epoxy molding compound.

INTRODUCTION

The National Technology Roadmap for Semiconductors targets "Measurement...of materials properties of packaging materials for the sizes, thicknesses, and temperatures of interest."(1) Due to the drive towards denser packages and the use of thin polymeric films as inner-layer dielectrics (ILDs), a technique is required that can make precision measurements of the coefficient of thermal expansion (CTE) of thin films. The current technique that is widely utilized by industry for determining the CTE of solid materials is thermomechanical analysis (TMA). However, the ASTM technique E 831-93 for CTE determination by TMA of solid materials calls for sample thicknesses between 2 mm and 10 mm.(2) These dimensions are far greater than those of interest as ILDs. A multi-user round-robin test compared the results obtained for the CTE of a 50 μm thick anisotropic polyimide film by TMA and a 1.1765 mm thick undoped, polished, <100> silicon. The results of this round-robin test clearly demonstrated that TMA is inadequate for the measurement of thin polymer films.(3) We have developed a technique utilizing a capacitance measurement for the accurate determination of the out-of-plane expansion of thin films on the order of 5 μm thick. This is important because the CTE is a key parameter for the design and reliability of polymer-containing products.(4)

Thermal expansion measurements have been performed on polymeric and non-polymeric materials, and hygrothermal expansion measurements have been performed on a bisphenol-A based epoxy with novolac hardener and fused silica filler.

EARLY ATTEMPTS AND CLAIMS

Due to the sensitivity of capacitance measurements, they have long been a technique for the measurement of small displacements. Resolution of capacitances to 1 nF/F are easily obtainable. Of the capacitance cells used for the measurement of polymeric films, most have problems that limit their reproducibility. Capacitance cell methods come in two general types: two-terminal and three-terminal methods. Of the two, the three terminal method has the least uncertainties.

The capacitance cell of Sao and Tiwary (5) was a two-terminal method that suffered from the problem of alignment of the electrodes plus expansion of the electrodes. The three-terminal method of Subrahmanyam and Subramanyam (6) suffers from several problems: electrode alignment, expansion and contraction of the entire apparatus, and the thermal spring constant which determines the loading conditions. Tong and coworkers (7) two-terminal technique suffers from electrode alignment problems, the requirement of specific specimen geometry, and stray capacitances and other fluctuations.
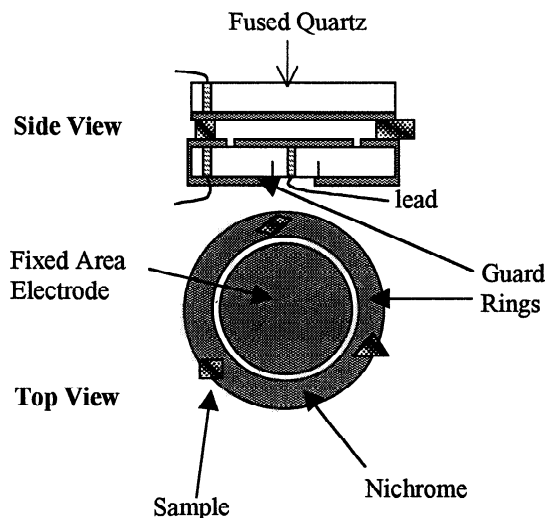
Our technique eliminates the problem of electrode alignment and uses the sensitivity of the three-terminal measurement. Previous measurements were reported on an earlier design (8) of our cell made from gold-coated Zerodur.(9)

EXPERIMENTS AND RESULTS

The absolute measurement technique that we have developed is based upon a parallel plate three-terminal guarded electrode. This technique derives from the well-known fact that the capacitance (C) of a parallel plate capacitor is given by:

$$C = \varepsilon \varepsilon_o A / d \qquad (1)$$

where ε is the dielectric constant of the material separating the plates (in the geometry of our experiment the material is air), ε_o is the permittivity constant ($\varepsilon_o = 8.854$ pF/m), A is the area of the plates, and d is the separation of the plates (which

FIGURE 1. Schematic of capacitance cell described in the text.

corresponds to the thickness of the material being measured).It should be recalled that a good three-terminal guarded electrode, if properly constructed, allows the area, A, to be independent of the position of the opposite electrode since the area is defined solely by the guarded electrode, as long as the opposing electrode is much larger than the diameter defined by the guard gap. Furthermore, for any easily realized guard gap, the effective area of the electrode varies only very slowly with a change in plate separation.(10)

Fig. 1 is an illustration of the capacitance cell that we utilized in obtaining our data. It should be noted that the electrodes have been made from fused quartz coated with nichrome to obtain an optically flat surface. Calibration of the expansion of the electrode area (A) was obtained by performing measurements on 2 mm Zerodur (9,11) spacers. The spacers were measured using a specially designed caliper with a resolution of ±0.2 μm.(12) Capacitance measurements were obtained with an Andeen-Hagerling 2500 A 1 kHz Ultra-Precision Capacitance Bridge with a 1 nF/F resolution.

Measurements were performed inside an environmental chamber with a dry air purge so that either thermal expansion (zero relative humidity and temperatures ranging from -25 °C to 180 °C) or hygrothermal expansion (0 to 85 % relative humidity with temperatures ranging from 25 °C to 100 °C) could be measured. The temperature of the cell was calibrated with a resistance temperature device (RTD) mounted to the cell with thermally conducting paste. The RTD was calibrated against an ITS-90 standard reference thermometer. Calibration of the humidity was performed by the dew point method.(14)

The following protocol was followed prior to each run. In a laminar flow hood equipped with a high efficiency particle arresting (HEPA) filter, the electrode surfaces were cleaned with ethanol and distilled water and dried with lens tissue. High pressure filtered air was used to remove any remaining particles from the surface. All samples were cleaned in the

same way. As is shown in Fig. 1, the samples were placed in the outside guard ring spaced $2\pi/3$ radians apart. The entire cell apparatus was then placed in a vacuum oven at 25 °C under 30 mm of Hg vacuum for 1 hour. (Evacuation of the cell was found necessary to simulate wringing, i.e., the removal of a trapped air layer caused by the contact of optically smooth surfaces.) The cell was then transferred to a Tenney (9) humidity/temperature chamber. The cell was equilibrated at the highest temperature of interest. Random temperatures were then sampled to eliminate any systematic errors induced by heating and cooling. The cell was allowed to equilibrate at any given temperature until the fluctuations in the capacitance were on the order of, or less than, 10^{-6} pF/pF. The pressure of the chamber was monitored during the run.

From the capacitance, the pressure, temperature, and relative humidity, the plate separation can be computed. Full details of the data analysis and reduction are given elsewhere.(13,14)
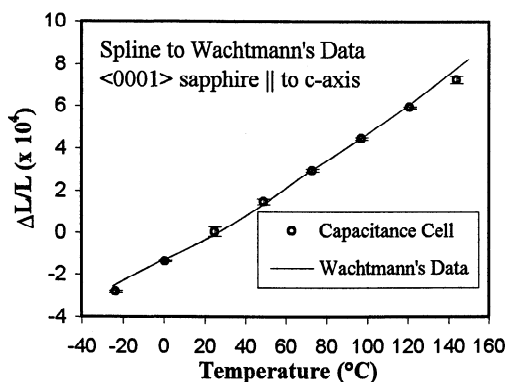
Thermal expansion measurements were performed on 0.5 mm <0001> single crystal sapphire and a 14 μm thick sample of a Dow Chemical Company's Cyclotene material. Swelling studies (hygrothermal expansion) were performed on a 1 mm thick epoxy molding compound - a bisphenol-A based epoxy with novolac hardener and fused silica filler. (This epoxy was obtained through National Semiconductor.)

RESULTS AND DISCUSSION

As discussed elsewhere (13), there are three levels in which the uncertainty in the thickness of the sample can be examined: [1] the isothermal stability as determined by measuring the sample's capacitance over long periods of time, e.g. 4 hours; [2] the reproducibility of the capacitance measurement determined by thermally (or hygrothermally) cycling the material and returning to the initial temperature; and [3] the reproducibility when measuring the capacitance after disassembling and reassembling the cell. The trend in magnitudes of the errors associated with each of the three above levels is [1]<[2]<<[3]. It is important to realize that the second level is the error that is associated with the measurement of the coefficient of thermal (or hygrothermal) expansion.
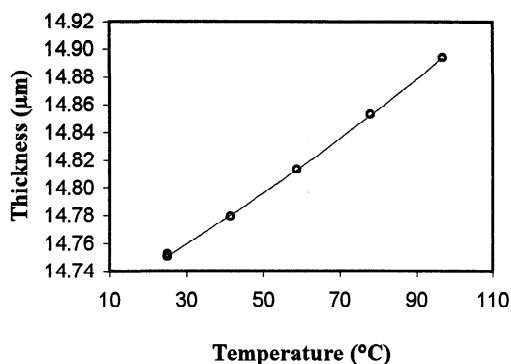
Aluminum Oxide (Sapphire)

The measurements on sapphire were performed to verify the ability of the technique to determine the CTE of a reference material. In Fig. 2, we have plotted $\Delta d/d_{25}$ for our experimentally determined data on <0001> sapphire. On the same graph, we have plotted the experimental data of Wachtman and coworkers (15,16) fitted to a cubic spline. Our data agrees well with the previous data. It should also be noted that Wachtman and coworkers used two different
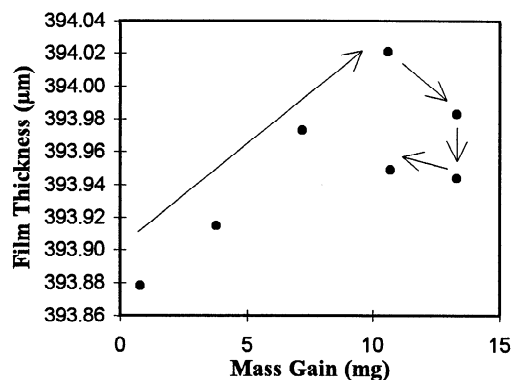
FIGURE 2. Expansion curve for single crystal <0001> oriented Al_2O_3 parallel to the principle axis. Note that the error bars correspond to the best estimate of two standard deviations in the experimental uncertainty.

experimental setups and the data were then matched at 25 °C. Examination of the data shows that the curvature in our data is much smoother than that of Wachtman and coworkers indicating that our data are more self consistent. One other fact which makes our data set superior to that of Wachtman and coworkers is that there is a temperature uncertainty of ±1.4 K associated with their data, whereas our data has a temperature uncertainty of ±0.2 K. It should be recalled that excluding problems associated with asperities, our technique gives the same relative resolution in thickness regardless of the absolute thickness. Therefore, the results are extendable to films with thickness on the order of 5 μm. Furthermore, sapphire has an expansion coefficient on the order of 3 μm/(m·K). Polymer films have expansion coefficients an order of magnitude larger and therefore are far easier to resolve.

Cyclotene

Figure 3. Expansion of the Dow Cyclotene as a function of temperature after subtraction of creep effects. The temperature profile followed was 100 °C, 25 °C, 60 °C, 40 °C, 80 °C, and 25 °C. (The manufacturer cites this Cyclotene's T_g as >350 °C.) The associated error bars are smaller than the size of the symbol.(12)

FIGURE 4. Epoxy thickness as a function of mass gain. Note the arrows indicate the direction in which the experiments were performed. The data points correspond to 2.2 %, 20 %, 40 %, 60 %, 60 %, and 40 %. The arrow pointing down at 13.3 mg mass gain corresponds to creep in the material with time. The associated errors bars are smaller than the size of the symbols. (12)

Because of the sensitivity of our technique, we were able to resolve creep of the sample at levels that ordinarily would not be observed. Therefore, the protocol that is given elsewhere was utilized to remove effects of creep for the Cyclotene.(13) To verify the consistency of the creep removal, the following temperature path was followed. Initially the sample was equilibrated at 150 °C for 20 hours. After the measured capacitance varied less than 1 μF/F the cell was equilibrated under the same circumstances for the following temperatures in the following order: 100 °C, 25 °C, 60 °C, 40 °C, 80 °C, and 25 °C. The data from each set was then corrected for creep and the curve in Fig. 3 was obtained. It is apparent from Fig. 3 that the data are self-consistent since all the data points fall on a single smooth curve. Additionally, the 25 °C point was reproduced within the experimental uncertainty.

Epoxy Molding Compound

The purpose of this paper has been to introduce the utility of our capacitance cell technique for various electronic packaging applications, therefore a full consideration of the behavior of the epoxy is beyond the scope of this work. (The reader is referred to Ref. 14 for further information.) A brief summary of the results and the implications are given here. In Fig. 4, we have plotted the film thickness as a function of the mass uptake of water. (It is important to note that mass uptake varied with humidity almost linearly.)

As can be seen from Fig. 4, the sample expands (swells) with increasing moisture uptake up to 40 %R.H. As the relative humidity was increased from 40 % to 60 %, two events were observed simultaneously. [1] The sample rapidly contracted, although the mass uptake increased, and [2] the

sample began to "creep", *i.e.,* the thickness decreased as a function of time. To verify that the first event was not creep, the humidity was decreased to 40 %. After equilibration, it was apparent that the sample expanded upon decreasing the relative moisture content from 13.3 mg (at 60 % relative humidity) to 10.7 mg (at 40 % relative humidity). Therefore, events one and two were separate. Further examination of this anomalous behavior is the subject of a future publication.

What is important to note is that this technique has the capability to resolve changes in film thicknesses on the order of 2 nm/mm caused by swelling. Furthermore, creep is observable at an order of sensitivity higher, *i.e.,* 2 nm/cm. Therefore, this technique has been demonstrated to have utility over a wide range of environmental conditions and can therefore address many of the concerns of the packaging industry.

CONCLUSIONS

In summary, we have developed an absolute, high sensitivity technique for the measurement of the z-axis expansion of thin films and optimized the measurement procedures for use by materials users and producers. This technique can easily provide the relevant CTE data to a higher accuracy than is currently available.

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