J Mater Sci (2007) 42:5686–5691
DOI 10.1007/s10853-006-0654-y

Thermal stress hysteresis and stress relaxation in an epoxy film

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Received: 3 January 2006 / Accepted: 7 July 2006 / Published online: 14 April 2007

Abstract Thermal cycling of an epoxy coating on silicon through the glass transition temperature (T_g) revealed a large stress hysteresis on the first thermal cycle through T_g and a change in the stress–temperature slope at T_g resulting from the change in the epoxy elastic properties due to the glass transition. This stress hysteresis was not observed on subsequent thermal cycles through T_g. However, after the coating was annealed (aged) below T_g (for hours or longer)—during which the stress relaxed exponentially with time—the stress hysteresis returned. The magnitude of stress hysteresis, on cycling through T_g, was found to correlate to the magnitude of long-time relaxation that occurred during annealing at temperatures below T_g.

Introduction

Epoxy films have many applications as encapsulates in microelectronics and MEMS devices and stress relief for improved reliability in flip chip interconnect arrays. Of significant concern is thermal stress development in epoxy that serves as a driving force for fracture in neighbouring ceramic layers [1, 2] and at epoxy–ceramic interfaces [3]. The mechanical requirements of the films include low cure temperature, small cure stress, small coefficient of thermal expansion (CTE), and thermal and mechanical stability.

Previous studies have demonstrated the effects of thermal viscoelastic stress development in epoxy films on deformation of microelectronic and MEMS devices [4–6]. Non-linear thermal-stress hysteresis events in free-standing polymer films [7] and polymer–substrate bilayers [8–13] have also been observed, although this hysteresis phenomenon is not fully understood. It is also known that this thermal-stress hysteresis occurs only on the first heating cycle, and subsequent thermal cycling results in a repeatable, overlapping thermal stress response, which is well-described by simple linear viscoelastic constitutive models [14]. This phenomenon has been termed "first-cycle hysteresis." First-cycle hysteresis events have not been incorporated in models of thermal stress development in microelectronics and MEMS devices.

Annealing of an epoxy resin at temperatures below T_g (physical aging), even in the fully cured state, results in enthalpic and stress relaxation, dependant on the anneal time and temperature [13, 15, 16]. During annealing below T_g the density, dielectric, and mechanical properties are all affected. In addition to internal stress changes, the enthalpy of the system also changes. However, these aging effects are completely reversible simply by heating the epoxy above its T_g. Extensive work in the area of aging effects on the thermal and physical properties of free standing, cured epoxy systems has been done by Monterrat and coworkers [15, 17, 18].

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The response of a thin epoxy coating on rigid substrate during thermal cycling and aging can be significantly different than the response in the bulk. The differences in the thermal expansion coefficient of the epoxy coating and the substrate materials can invoke stresses in the coating. Additional stresses can be imparted into the sample as the coating tries to contract due to an increase in the density during the curing and aging processes. Perera [11–13] has extensively studied the physical aging of epoxy and other glassy coatings.

This work examines the stress–temperature behaviour of an epoxy film during thermal cycling. The effects of repeated cycling and annealing at temperatures below T_g (aging) on the thermal-stress hysteresis are reported. A relationship between first-cycle hysteresis and stress relaxation during aging is identified and a simple procedure to identify the thermal-stress hysteresis and predict its response to annealing time is presented.

Experimental description

A modified flexibilized delayed cationic cure epoxy resin was spin-coated on a 4″ (100) Si wafer (200 µm thick) at 6,000 rpm for 30 s. The 150-µm thick epoxy film was immediately UV-cured in air at 400 mW/cm^2 for 1 s then thermally cured in air at 120 °C for 10 min, conditions previously found by FTIR to cause 98% or more cure on similar samples. The coating was exposed to ambient laboratory (20 °C, 40% relative humidity) conditions for 1 day prior to thermal cycling experiments. Curvature measurements were performed during thermal cycling at 1 °C/min under N_2 flow with a commercial tool (Tencor Flexus FLX2320). The film was exposed to the following temperature history: cycled between 30 and 95 °C three times, annealed at 30 °C for 1 h (aged), cycled between 30 and 95 °C three times, annealed at 30 °C for 5 h, cycled between 30 and 95 °C three times, annealed at 30 °C for 24 h, then cycled between 30 and 95 °C three times. Film stress was calculated with the following simplification of Timoshenko's bi-material beam analysis [19] commonly attributed to Corcoran [20]:

$$\Delta\sigma = \Delta\kappa \frac{E_s}{1 - \nu_s} \frac{t_s^3}{6(t_s + t)t} \tag{1}$$

where $\Delta\kappa$ is the change in substrate curvature, $\Delta\sigma$ is the change in epoxy stress, t_s is the substrate thickness, t is the epoxy thickness, $E_s/(1 - \nu_s)$ = 180.5 GPa [21] is the substrate biaxial modulus (where E_s is Young's Modulus and ν_s is Poisson's Ratio). Equation 1 is applicable for coatings of arbitrary thickness that have a Young's modulus much less than the substrate Young's modulus and can easily be derived from the more complicated expression in [22] by assuming $E_f/E_s \ll 1$, where E_f is the coating Young's modulus. The sign convention used here is that a positive stress corresponds to tensile stress and negative stress corresponds to compressive stress. The relevance of Eq. 1 for non-linear deformations is addressed in Appendix A.

Experimental results and discussion

Figure 1 shows the thermal stress response of the epoxy film. The point labelled "Start" is the tensile cure stress measured at room temperature, 1 day after curing. The first heating cycle from 21 to 95 °C has three characteristics: (1) a steep negative slope indicating an epoxy coefficient of thermal expansion (CTE) greater than that of the Si substrate, (2) a transition to positive slope, and (3) a shallow negative slope. Outside of the transition region (2), the stress–temperature behaviour can be described by:

$$\Delta\sigma(T) = \int_{T_1}^{T_2} \frac{E_f}{1 - \nu_f} (\alpha_f - \alpha_s) \mathrm{d}T \tag{2}$$

where $\Delta\sigma$ is the change in stress from temperature T_1 to temperature T_2, $E_f/(1 - \nu_f)$ is the film biaxial modulus, α_s is the substrate CTE, and α_f is the film CTE. The magnitude of the stress–temperature slope is controlled by the CTE mismatch between the film and substrate and the film biaxial modulus. Although

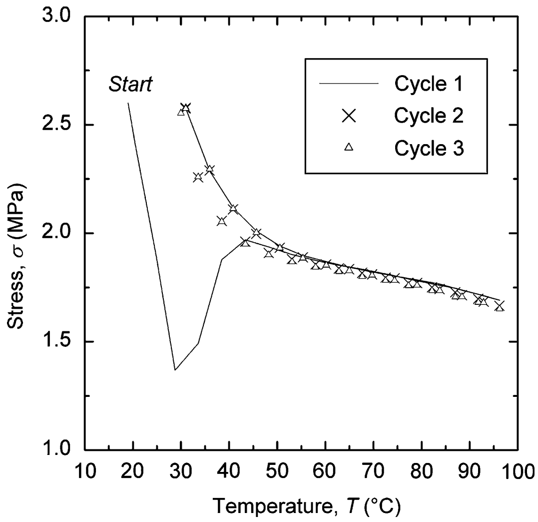

Fig. 1 Thermal stress response of epoxy film on Si substrate

independent measurements of Young's modulus and CTE are not available, it is well known that Young's modulus decreases and CTE increases at temperatures above T_g. Thus the change in slope from region (1) to region (3) can be attributed to the film Young's modulus decrease above T_g. (The film CTE increases above T_g, but not enough to exceed the Young's modulus increase.)

On cooling from 95 to 50 °C, the stress response returned along the same path as the heating cycle. At 50 °C the slope magnitude increased but remained less than the slope magnitude of the initial heating data at 30 °C. As a result of the thermal history, the stress at 30 °C is now more tensile than during the first heating cycle (first-cycle hysteresis). The thermal stress hysteresis is quantified here as the stress at 30 °C on cooling after the first cycle through T_g, minus the stress at 30 °C on the first heating cycle. The hysteresis in Fig. 1 is 1.2 MPa. Subsequent cycling (shown as symbols in Fig. 1) revealed a closed-loop hysteresis. The closed-loop hysteresis is a viscoelastic phenomenon resulting from a delay of the material response to the change in temperature. The stress–temperature relationship followed the same path as the first cooling cycle, similar to previous observations of cycling through T_g [8–10, 23]. The presence of a first-cycle thermal-stress hysteresis in the un-aged coating was not observed in similar studies [11–13]. Instead, in the referenced studies the coated sample was heated above its T_g for an extended period of time to eliminate any aging effects (de-aging). It is felt that this initial above-T_g heating cycle would also eliminate the stresses imparted into the coating during the curing (or cross-linking) process, such as were seen in the samples examined in this report.

The T_g was estimated by the point of intersection from a linear fitting of the thermal stresses from 30 to 40 °C and 50 to 100 °C (excluding the first heating cycle) [12]. A glass transition temperature of approximately $T_g = 40.2$ °C was obtained (and can be compared to a T_g of 44.3 °C obtained by differential scanning calorimetry).

The cured epoxy coating, on a silicon substrate, was annealed at 30 °C (aged) for 1 h, and then cycled again through the thermal history described above. The stress–temperature response during cycling is shown in Fig. 2. The first-cycle hysteresis was significantly reduced relative to that shown in Fig. 1 (from 1.2 to 0.11 MPa), while the stress–temperature slopes above and below T_g on subsequent thermal cycling remained practically unchanged, relative to the un-aged thermal cycles in Fig. 1. The stress hysteresis observed in the first thermal cycle after aging, for a cross-linked organic coating, has been observed elsewhere [11, 13]. The differences in stress values in the first thermal cycle of the aged samples, relative to subsequent thermal cycles, is attributed mainly to the thermal stress relaxation occurring during the isothermal heating below T_g (i.e., physical aging process) [13]. A dramatic reduction in the first thermal cycle hysteresis stress values was observed in the aged sample compared to the un-aged sample. This stress reduction is attributed to the relaxation of some of the stresses that were imparted into the sample during the curing process.

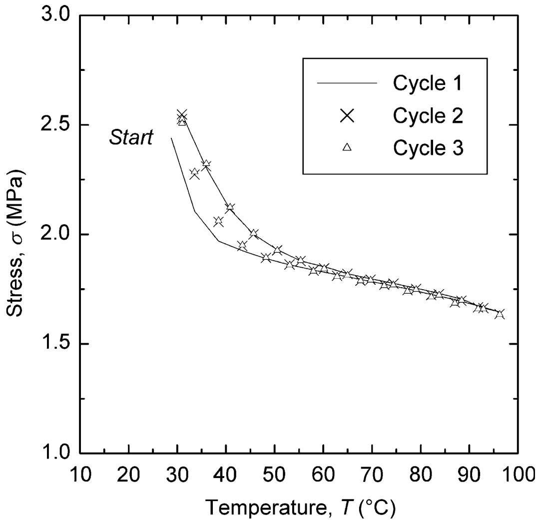

Fig. 2 Thermal stress response of epoxy film on Si substrate 1 h (at 30 °C) after the cycling shown in Fig. 1

The film–substrate system was then held at 30 °C (aged) for 5 and 24 h, exposed to the same thermal cycling between each hold. The stress–temperature behaviour from cycling after the 5 h anneal and 24 h anneal is shown in Figs. 3 and 4, respectively. The first-cycle hysteresis increased after the 5 h anneal, relative to the 1 h anneal (Fig. 2), from 0.11 to 0.2 MPa. After the 24 h anneal at 30 °C the hysteresis further increased to 0.44 MPa. The stress–temperature slope below T_g after aging for 24 h was steeper than the stress–temperature slope below T_g subsequent to heating above T_g (de-aging). This may be a result of an increase in Young's modulus of the coating with aging time (the coefficient of thermal expansion is expected to decrease with aging time, but not sufficiently to overcome the increase in modulus) [13].

The first thermal cycles from Figs. 1 and 4 are compared in Fig. 5. The temperature at which the transition (from a steep negative slope to a positive slope) occurred increased by 10 °C after the 24 h hold, and the stress at which this transition occurred also

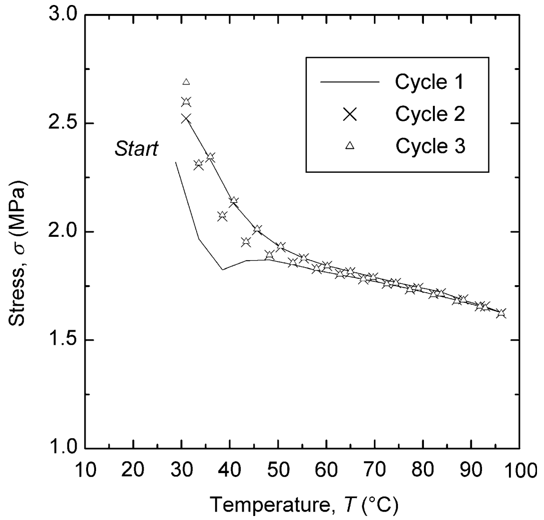

Fig. 3 Thermal stress response of epoxy film on Si substrate 5 h (at 30 °C) after the cycling shown in Fig. 2

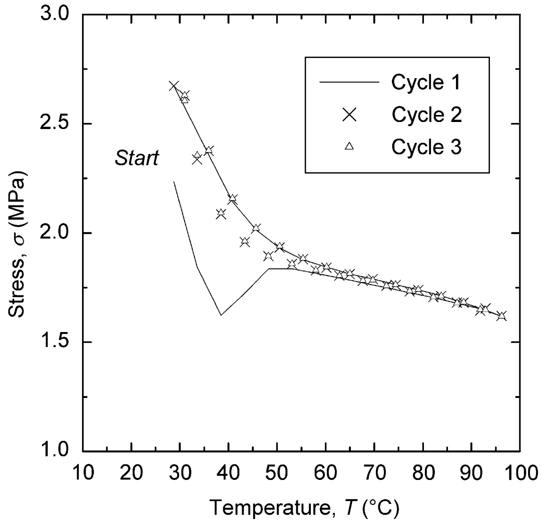

Fig. 4 Thermal stress response of epoxy film on Si substrate 24 h (at 30 °C) after the cycling shown in Fig. 3

increased by 0.26 MPa. An increase in glass transition temperature with aging has been observed elsewhere [11, 13, 18, 24]. The magnitude of the stress has been reported to be dependent on both the aging temperature and time [11, 13]. Although aging temperature was not examined in this work, the increase in the magnitude of the stress with increasing aging time was also observed in this study. The change in stress during the 1, 5, and 24 h holds, at 30 °C, was approximated to be exponential with time, as shown in Fig. 6. The exponential decay of internal stresses has been observed in epoxy films during annealing at constant temperatures below T_g [13, 25]. Like the first-cycle hysteresis, the stress relaxation during aging has been attributed to the approach of the glassy coating to thermodynamic equilibrium [11–13].

The stress relaxation observed in this study during sub-T_g aging is attributed to the structural changes that occur in the epoxy coating as it approaches thermodynamic equilibrium. As a thermoset is cooled through its T_g, and into the glassy state, it is in a thermodynamic non-equilibrium. Volume and enthalpy relaxation occurs simultaneously during the aging process resulting in significant thermal and mechanical property changes [11, 13, 15, 16]. The stress relaxation process during aging has been shown to be affected by both aging temperature and time, and is attributed to changes in chain mobility [13].

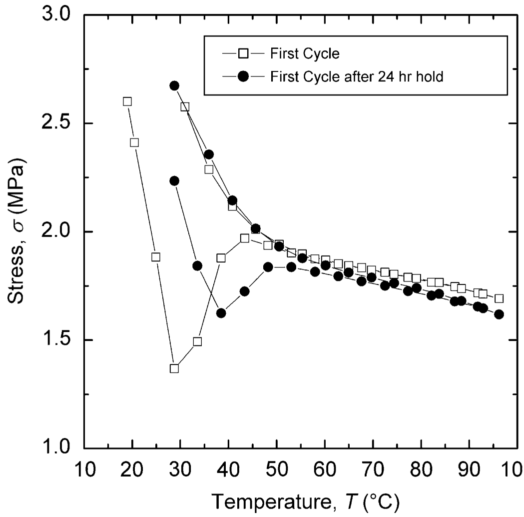

Fig. 5 Comparison of the first cycles from Figs. 1 and 4

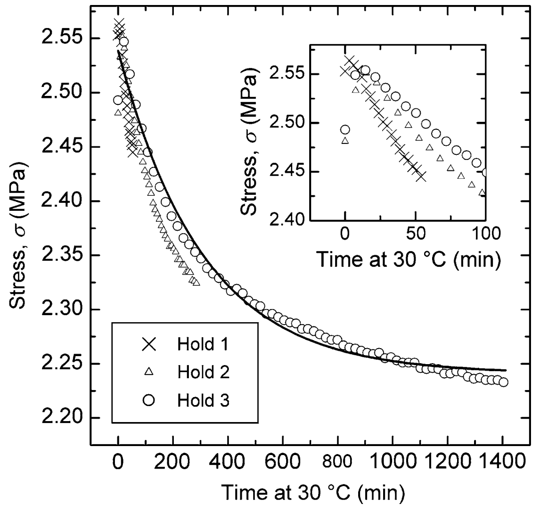

Fig. 6 Stress relaxation at 30 °C after thermal cycling. The solid line is an exponential fit to Hold 3 data: $\sigma(t) = 2.24 + 0.3 \exp(-t/309)$

The rate of stress relaxation during the first 50 min was greatest for the first hold, less for the second hold, and least for the third hold. This is an unexpected observation, as the stress relaxation time constants are expected to be completely reversible after de-aging. The magnitude of stress relaxation during aging appears to decrease with increasing cumulative aging time. The inset shows that the stress actually became more tensile during the first 10–20 min of the hold, prior to relaxing. Like the closed-loop hysteresis on the second and third thermal cycles, the small increase in stress at the start of the hold, at 30 °C, is thought to be a viscoelastic effect due to the delay between the change in temperature and the material's response [26].

Figure 7 shows a plot of the first-cycle hysteresis as a function of the stress relaxation (during holds at 30 °C). A linear relationship between the first-cycle stress hysteresis and stress relaxation, as a function of aging time, was found with the magnitude of both stresses increasing with longer aging times. This is the first time the authors are aware of that a relationship between the first-cycle thermal-stress hysteresis and stress relaxation of aged epoxy coatings has been reported.

For aging experiments performed at 30 °C, Figs. 6 and 7 can be used to estimate the stress hysteresis for a given amount of annealing time. Neglecting the apparent dependence of stress relaxation rate on cumulative aging time, the stress relaxation during aging at 30 °C can be estimated from the exponential fit to the Hold 3 data in Fig. 6: $\sigma_r(t) = 2.24 + 0.3 \exp(-t/309)$, where t is the anneal time. Second, first-cycle hysteresis can be estimated from the linear fit to the data in Fig. 7: $\Delta\sigma(t) = -0.08 + 1.76\ \sigma_r(t)$. It should be noted that these equations were fitted to aging experiments performed at 30 °C, other fitting parameters may be required if other annealing temperatures are used. Using this technique, first-cycle hysteresis can now be easily incorporated into structural models, just as stress relaxation during aging is already incorporated into enthalpic models [15]. Stress relaxation and the first-cycle thermal-stress hysteresis will likely also have temperature dependences, which will be studied in the future [11, 13].

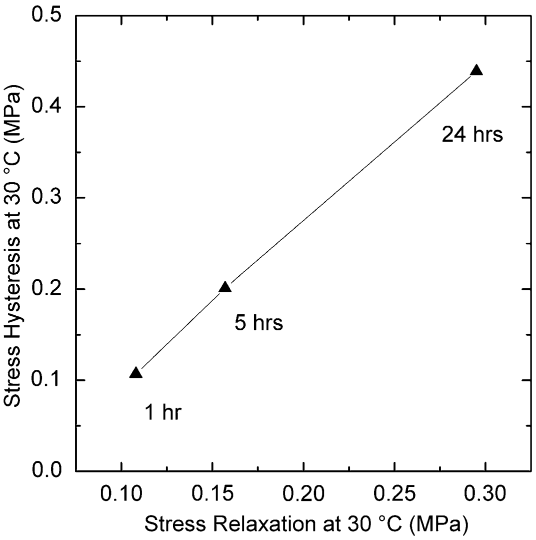

Fig. 7 The stress hysteresis at 30 °C is linearly correlated to the stress relaxation during holding at 30 °C. The least-squares slope and intercept are 1.76 and –0.08 MPa, respectively

Summary

First-cycle stress hysteresis was examined in an epoxy coating that was thermally cycled through T_g, and was correlated to stress relaxations below T_g (physical aging) and significant changes in the stress–temperature behaviour.

1. The stress hysteresis was observed in an epoxy film during the first thermal cycle through T_g, but was absent on subsequent cycles through T_g. After the polymer was annealed below T_g (aged) for 1 h or more the stress hysteresis returned, although with reduced magnitude.
2. During annealing below T_g (aging) the coating stresses relaxed exponentially. A correlation was found between the amount of stress relaxation and the magnitude of the first-cycle stress hysteresis, on subsequent cycling through T_g.
3. A technique to estimate the stress hysteresis after arbitrary hold times, at a constant temperature below T_g, was introduced.

Acknowledgement The author (JT) acknowledges Awirut Maglai for assistance with sample preparation and Bob Matz for helpful discussions.

Appendix A: Non-linear deformation analysis

The use of Eq. 1 requires that the strains and rotations in the system be infinitesimally small. This requirement was examined using the analysis of Freund et al. [27], who showed that non-linear deformation effects can be avoided if the dimensionless parameters S or K are less than 0.3–0.4 or 0.2, respectively:

$$S = 1.5\varepsilon_m R^2 t \frac{(1-\nu_s)E_f}{(1-\nu)E_s t_s^3} \tag{A1}$$

and

$$K = 0.25R^2 \frac{\Delta\kappa}{t_s}, \tag{A2}$$

where ε_m is the imposed thermal mismatch strain, R is the sample radius (50 mm), E_f is the film Young's Modulus, and v is the film Poisson's Ratio. Since the film mechanical properties are not known, the parameter K was evaluated using the largest change in curvature observed over the course of the experiment, $\Delta\kappa = 0.02\ \mathrm{m}^{-1}$, to be $K = 0.016$. As $K < 0.2$, non-linear deformations were not considered.

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