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# Thermal Cycling Effects on Critical Adhesion Energy and Residual Stress in Benzocyclobutene-Bonded Wafers

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The effects of thermal cycling on critical adhesion energy and residual stress at the interface between benzocyclobutene (BCB) and silicon dioxide (SiO<sub>2</sub>) coated silicon wafers were evaluated by four-point bending and wafer curvature techniques. Wafers were bonded using BCB in an established (baseline) process, and the SiO<sub>2</sub> films were deposited by plasma-enhanced chemical vapor deposition (PECVD). Thermal cycling was done between room temperature and a peak temperature. In thermal cycling performed with 350 and 400 °C peak temperatures, the critical adhesion energy increased significantly during the first thermal cycle. The increase in critical adhesion energy is attributed to relaxation of residual stress in PECVD SiO<sub>2</sub>, which in turn is attributed to condensation reactions in those films. Thermal cycling also cures the BCB beyond the ~88% achieved in the baseline process, and the residual stress in the BCB is reset at a glass transition temperature corresponding to the increased BCB cure conversion. As more thermal cycles are performed, stress hysteresis in the BCB decreases as the cure stabilizes at 94-95%. © 2005 The Electrochemical Society. [DOI: 10.1149/1.1869252] All rights reserved.

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Wafer-level three-dimensional (3D) integration is an emerging technology to increase interconnect performance and functionality of integrated circuits (ICs).<sup>1-8</sup> In one approach to wafer-level 3D integration, fully processed wafers (with multilevel on-chip interconnects) are aligned and bonded with a dielectric glue, followed by thinning one of the wafers to less than 10  $\mu$ m using mechanical grinding, chemical mechanical planarization (CMP), and wet etching. Subsequently, interwafer interconnects are formed using a copper damascene patterning process.<sup>5-8</sup>

The bonds in the 3D wafer stacks must have sufficiently high critical adhesion energies and low residual stresses in order to resist the impacts of subsequent processing steps such as grinding, CMP, and thermal cycling. We have considered several low-k dielectric polymers as bonding glue candidates, have developed a baseline wafer bonding process using benzocyclobutene (BCB), and have evaluated the critical adhesion energy and residual stress when using BCB to bond various stacked layers.<sup>5,6</sup> BCB is used for wafer-to-wafer bonding because of the high critical adhesion energy and high fraction of bonded area (nearly 100% on 200 mm wafers) as previously reported.<sup>5,9,10</sup>

During postbonding processing, the 3D wafer stack undergoes multiple thermal excursions and high-temperature processes (for the purposes of this paper, over 350°C). Example processes are etching of interwafer vias, deposition and annealing of copper used to form the interwafer interconnections, curing of subsequent BCB layers when adding wafers to the stack, and subsequent packaging processes.<sup>11-13</sup> Thus, it is critical to understand the effects of high-temperature thermal cycling on the wafer stacks. A large part of the concern about high-temperature thermal cycling relates to the evolution of the critical adhesion energy and residual stress of the bonded interfaces. Thermal cycling of BCB-bonded layers may cause an increase in critical adhesion energy by release of residual stress. Thermal cycling may cause adhesive failure at the interface between BCB and adjacent layers, or cohesive failure within the BCB layer.<sup>14</sup> Although BCB has been used in microelectronic applications in the back-end-of-the-line (BEOL), packaging, and 3D integration processes, the effects of the multiple and high-temperature thermal excursions on critical adhesion energy and residual stress at bonding interfaces and on the physical stability of BCB are not well understood. Most published studies consider the effects of thermal cycling of BCB in a low-temperature range  $(-125 \text{ to } 150^{\circ}\text{C})$ ,<sup>15,16</sup> and the critical adhesion energy at the interface between BCB and wafer has mostly been evaluated qualitatively using "stud pull" or "scotch tape" tests.<sup>17,18</sup>

In this work, we report on increases in critical adhesion energy between BCB and plasma-enhanced chemical vapor deposition (PECVD) silicon dioxide (SiO<sub>2</sub>) coated silicon wafers due to hightemperature thermal cycling. Such changes in adhesion energy might play a large role in wafer-level 3D IC technology platforms. We describe a phenomenological model that relates the increase in the critical adhesion energy to decreases in residual stress in PECVD SiO<sub>2</sub> layers which result from condensation reactions. We also report on the thermal stability of the BCB using thermal cycling tests performed in the temperature range 350-450°C in nitrogen ambients.

## **Processing and Characterization**

BCB and PECVD SiO<sub>2</sub> layer deposition.—The thermal cycling tests reported in this paper are performed with four different wafers or wafer stacks: (*i*) silicon wafer covered with 1  $\mu$ m PECVD SiO<sub>2</sub>; (*ii*) silicon wafer coated with 3  $\mu$ m BCB; (*iii*) silicon wafer covered with 1  $\mu$ m PECVD SiO<sub>2</sub> followed by 3  $\mu$ m BCB; and (*iv*) a bonded wafer pair consisting of a 2.6  $\mu$ m thick BCB layer sandwiched between two silicon wafers, each covered with 1  $\mu$ m PECVD SiO<sub>2</sub> layer. The 200 mm silicon wafers used are about 730  $\mu$ m thick. PECVD SiO<sub>2</sub> layers are deposited using SiH<sub>4</sub> and N<sub>2</sub>O at 300°C in a Plasmatherm 73 (Plasma-Therm Inc., Voorhees, NJ) with a chamber pressure of 0.9 Torr and radio frequency (13.56 MHz) power of 25 W. The desirable overall reaction during this deposition process is

$$SiH_4 + 2N_2O \rightarrow SiO_2(s) + 2H_2 + 2N_2$$
<sup>[1]</sup>

The thicknesses of PECVD  $SiO_2$  layers are measured using both spectroscopic reflectometry and ellipsometry. The standard deviation of the measured thickness across a wafer is less than 5%.

Adhesion promoter (AP3000, Dow Chemical) and BCB resin (Cyclotene 3022-45, Dow Chemical) are spin-coated on wafers (*ii*) and (*iii*) listed above after precleaning with a solution of sulfuric acid and hydrogen peroxide, followed by spin-dry cleaning. Spin-coatings are done in a FlexiFab spin coater (Machine Technology Inc., Ventura, CA) that includes a hot plate for heat-treating wafers in either a nitrogen or room air ambient. After spin-on of 20 nm of adhesion promoter,<sup>19</sup> and spin-on and baking of BCB, curing is

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Figure 1. Beam specimen geometry for four-point bending experiments.

performed using the same procedure as used in the baseline bonding process, except without pressurization.<sup>5</sup> The spun-on BCB is baked at 170°C and cooled with a nitrogen environment in the FlexiFab. The standard deviation of BCB thickness across a wafer after curing (measured using spectroscopic reflectometry and ellipsometry) is less than 1%. The critical adhesion energy of wafers bonded using the adhesion promoter is higher than that of wafers bonded without the adhesion promoter.<sup>6</sup> This is attributed to reactions between the adhesion promoter, BCB resin, and PECVD oxide.<sup>14</sup>

*Wafer bonding.*—Wafer contact and bonding are conducted using an EVG EV501 wafer bonder (EVGroup, Inc., Schaerding, Austria). After two wafers, both of which are coated with BCB, are mounted on the bonder chuck and placed in the bonder, the bond chamber is pumped down to  $2 \times 10^{-4}$  mbar and the wafers are heated at a ramp rate of  $32^{\circ}$ C/min. When the predetermined temperature (250°C) is reached, the wafers are pressed together with a uniformly distributed down force of 10,000 N (~0.3 MPa) for 1 h. The final temperature and heating time are determined by the desired extent of curing of the BCB, because the BCB cure reaction is key to bonding between the glue and its adjacent layers, as well as at any glue-glue interface. After the bonding process, the pressure is released and the wafer pair is cooled.

*Critical adhesion energy measurement.*—Critical adhesion energy is estimated using four-point bending experiments. Four-point bending is based on a theory of fracture mechanics presented by Charalambides *et al.*,<sup>20,21</sup> where delamination is modeled as a crack propagating along the interface between two materials.<sup>22</sup> In that research, the critical adhesion energy of a bimaterial interface was deduced analytically by evaluating the difference in the strain energy between the uncracked and cracked beam samples. We use their formula to calculate the critical adhesion energy of corresponding interfaces. The effect of residual stress on critical adhesion energy has been studied by several research groups. Suo and Hutchinson<sup>23</sup> proposed the effect of residual stress of a bi-material interface on critical adhesion energy, and Sha *et al.*<sup>24</sup> reported the effect of residual stress on critical adhesion energy.

Each beam specimen used with the four-point bending is prepared from wafers or pieces of wafers that have undergone any and all processing steps. Specimens are prepared by dicing the processed wafer pieces to the nominal dimensions of 40 mm long, 4 mm wide, and 1.5 mm thick, followed by precrack formation and chemical treatment (Fig. 1). The precrack is formed by sawing partially (mostly) through one of the wafers.<sup>14</sup> After precrack formation, the specimen is wet-etched in order to: (i) smooth damaged and roughened surfaces that are produced during precrack formation, and (*ii*) etch the precrack until it reaches the glue interface.<sup>14</sup> This silicon etch is critical in order to obtain reproducible load plateaus. With the beam specimen mounted in a special fixture shown in Fig. 2 (Zwick T1-FR005TN Material Testing Machine), a load cell measures the applied load and an actuator measures displacement. The load vs. displacement curve generated during this process is the basis for critical adhesion energy estimates. A typical load vs. displacement curve is shown in Fig. 3. As the load is applied, the sample deforms elastically and the precrack propagates to the weak interface, which is "below" the precracked silicon. The data that represent this form



Figure 2. Photo of the four-point bending apparatus (Zwick T1-FR005TN).

a straight line on the load-displacement curve. At sufficiently high load, the crack proceeds along the weak interface and the load reaches a load plateau,  $P_c$ , in the load-displacement curve. The load plateau indicates that the adhesion energy released per unit area is independent of the crack length. Applying beam theory with the load plateau value, the critical adhesion energy,  $G_c$ , can be estimated using<sup>20</sup>

$$G_{\rm c} = \frac{3(1-\nu_2^2)P_{\rm c}^2 l^2}{2E_2 b^2 h^3} \left[ \frac{1}{\eta_2^3} - \lambda \left/ \left( \eta_1^3 + \lambda \eta_2^3 + 3\lambda \frac{\eta_1 \eta_2}{\eta_1 + \lambda \eta_2} \right) \right]$$
[2]

where  $E_1$  and  $\nu_1$  are Young's modulus and Poisson's ratio of the precracked wafer, and  $E_2$  and  $\nu_2$  are Young's modulus and Poisson's ratio of the uncracked wafer,  $\lambda$  is the effective modulus, *i.e.*,  $E_2(1 - \nu_1^2)/E_1(1 - \nu_2^2)$ ,  $P_c$  is the load plateau value, l is the spacing between inner and outer loading pins, and b is the specimen width.  $\eta_1$  is the ratio of the cracked wafer thickness,  $h_1$ , to the entire bonded wafer thickness,  $h_1 + h_2$ , and  $\eta_2$  is the ratio of the uncracked wafer thickness,  $h_1 + h_2$  (see Fig. 1).

For all results reported here, at least three samples were tested. The standard deviation of the adhesion energy determined using four-point bending is less than 7% of the average value. Four-point bending results depend upon uncertainties introduced by sample preparation and measurement procedures. While the relative contri-



**Figure 3.** A typical load-displacement curve for measuring saturation load value. In the early stage of load, the upper loading pins adjust themselves to keep the load balanced, and then load is applied to the beam sample. Thus, although the initial displacement coordinate is 0, the initial load is not 0. This load *vs.* displacement curve has four distinct regions. The linear elastic region comes from pure bending of precracked and uncracked substrates (range 1). The crack kink region occurs due to movement of the initial precrack spot into the weak interface (range 2). The plateau load—steady-state crack propagation (range 3) region indicates crack propagation along the bonding interface. The second linear elastic region (range 4).



**Figure 4.** Beam specimen configurations and critical adhesion energy for one, five, and ten thermal cycles at peak cycle temperature of 350, 400, and 450°C. BCB layer is sandwiched by PECVD oxide-coated silicon wafers (see Table I).

butions of sample preparation and measurement uncertainties are not well established, the values of the total standard deviations are reasonable.

Residual stress measurement and analysis.—Residual stresses (taken here as the sum of intrinsic and coefficient of thermal expansion (CTE)-mismatch-induced stresses) in PECVD oxide and BCB films deposited on silicon wafers are estimated by measuring wafer curvature.<sup>25</sup> Stress evolutions in PECVD oxide layers during thermal cycling reported by Thurn and Cook<sup>26</sup> and Chen *et al.*<sup>27</sup> are used as a basis for interpreting our stress results. Thurn and Cook<sup>26</sup> reported on stress release in PECVD oxide films during thermal cycling using an analysis that incorporates both intrinsic and thermal components of the net stress. Chen *et al.*<sup>27</sup> reported on changes in the density of PECVD oxide films during thermal cycling and connects those changes with changes in chemical compositions within the oxide film.

Residual stress due to a film deposited on a substrate (a silicon wafer in this study) is determined by measuring the deformation of the substrate using

$$\sigma = \frac{E_{\rm s}}{1 - \nu_{\rm s}} \frac{t_{\rm s}^2}{6t_{\rm f}} \left(\frac{1}{R} - \frac{1}{R_0}\right)$$
[3]

where  $E_s$  and  $v_s$  are Young's modulus and Poisson's ratio for the substrate,  $t_s$  and  $t_f$  are the substrate and film thicknesses,  $R_0$  is the radius of curvature of the starting silicon wafer before film deposition, and R is the radius of curvature of the sample after film deposition (room temperature) or during thermal cycling (from room temperature to peak temperature).<sup>28</sup> Both  $R_0$  and R are estimated by scanning a laser beam across the sample and measuring the angle of the reflected beam. A Tencor FLX-2320 system (Tencor Instruments, Mountain View, CA) is used to measure curvature R *in situ* as a function of ambient temperature (peak temperature, ramp rate, and laser beam scan interval are described later). After R is estimated, the stress  $\sigma$  is computed by the Tencor software, which uses Eq. 3. The chamber of the FLX-2320 system consists of a heater and a laser beam and is connected with a nitrogen tank, so that thermal cycling and laser scanning of samples can be conducted in a nitrogen ambient. During temperature ramping and the dwell time at the

peak temperature, wafer curvature is measured along one diameter. For consistency, the radius of curvature is measured using laser deflection data taken along the diameter that is perpendicular to a line drawn from the notch to the opposite side. Stress *vs.* temperature scans were done on two samples for each reported result and the results were found to be very similar in each case.

Thermal cycle conditions.—Thermal cycling tests are performed with rectangular-shaped pieces (nominal dimensions of 40  $\times$  30 mm) cut from the wafers. After thermal cycling, each rectangular shape is diced again into beam specimens (nominal dimensions of 40  $\times$  4  $\times$  1.5 mm) and four-point bending tests are performed.

Several variables can be changed in thermal cycling tests. The effects of the number of cycles and peak cycle temperature on critical adhesion energy and residual stress are investigated in this work.<sup>25</sup> One, five, and ten thermal cycles (labeled as 1-, 5-, and 10-cycle) were chosen, because preliminary experiments indicated that the residual stress and critical adhesion energy both reached a saturation point in less than ten cycles. Peak cycle temperatures of 350, 400, and 450 °C were chosen after considering potential subsequent 3D IC processes (such as deep via etching and barrier metal/copper filling for forming vertical interwafer interconnects), subsequent packaging processing, and reported thermal stability results of BCB.<sup>19,29</sup>

A nitrogen ambient is used during the thermal cycling to prevent oxidation of BCB. A ramp rate (both ramp-up and cool down) of  $25^{\circ}$ C/min was used, with a dwell time of 20 min at the peak temperature. The FLX-2320 system returned curvature data three times per minute during temperature ramping and once every 2 min during the dwell time at the peak temperature.

Fourier transform infrared spectroscopy.—Chemical properties of bulk PECVD oxide layers before and after thermal cycling were examined by measuring the absorbance of the different oxide layers using Nicolet MAGNA 560 Fourier transform infrared spectroscopy (FTIR; Nicolet, Madison, WI) over a wavelength range of 400 -4000 cm<sup>-1</sup>. These data were used to evaluate the condensation reaction in PECVD oxide films (discussed below) during thermal cycling. All spectra were recorded at a resolution of 4 cm<sup>-1</sup> and averaged over 512 scans. The analysis chamber is continuously pumped down (vacuum is applied) to reduce the influence of water vapor. FTIR samples were nominally  $10 \times 10$  mm pieces cut from oxidecoated silicon wafers that had undergone various thermal treatments. They were mounted perpendicular to the incident IR beam. Transmission through oxide-coated silicon wafers was measured and then the absorption of the silicon wafer is subtracted to obtain IR data of the oxide layers.

Spectroscopic ellipsometry.—Thicknesses of PECVD oxide and BCB were measured with an M-44 variable angle spectroscopic ellipsometry (VASE) instrument (J.A. Woollam Co., Lincoln, NE). Through spectroscopic scans, ellipsometric data were taken at three incidence angles. For both PECVD oxide and BCB layers, incidence angles of  $65^{\circ}$ ,  $70^{\circ}$ , and  $75^{\circ}$  were used.<sup>30,31</sup> Before measuring the thicknesses of PECVD oxide or BCB on silicon, the VASE standard silicon wafer was calibrated and aligned at an incident angle of  $70^{\circ}$ .

Table I. Critical adhesion energy dependence of number of cycles and peak temperatures for Si/SiO<sub>2</sub>/AP/BCB/AP/SiO<sub>2</sub>/Si (structure depicted in Fig. 4).<sup>a</sup>

Before cycling			350°C				400°C				450°C		
n	$G_{\rm c}$ $({ m J/m^2})$	S.D. (J/m <sup>2</sup> )	Cycles	n	$G_{ m c} \ ({ m J/m^2})$	S.D. (J/m <sup>2</sup> )	Cycles	n	$G_{ m c} \ ({ m J/m^2})$	S.D. (J/m <sup>2</sup> )	Cycles	п	$G_{\rm c}$ $({ m J/m^2})$
			1	4	36	1.8	1	4	41	2.7	1	3	< 0.5
6	31	1.7	5	4	37	2.1	5	4	41	2.3	5	3	< 0.5
			10	4	37	2.3	10	4	42	2	10	3	< 0.5

<sup>a</sup> n is number of samples;  $G_c$  is mean value of critical adhesion energy; and S.D. is standard deviation of  $G_c$ .



**Figure 5.** Geometry of stacked layers and temperature dependence of residual stress of the stacked layers during the first and second thermal cycles: (a) peak temperature of 350 and (b) 400°C.

After the standard wafer calibration, ellipsometric data of PECVD oxide and BCB were obtained using the three incidence angles. The ellipsometric data of both were then analyzed using the VASE software package (J.A. Woollam Co.), which is based on a least-square regression analysis to obtain the unknown fitting parameters.<sup>31</sup> The fitting parameters are varied to minimize the differences between the measured values and calculated values from the ellipsometric angles by using the defined optical model and the ellipsometric equations. From the applied ellipsometric equations, thicknesses of PECVD oxide and BCB layers are obtained.

#### **Results and Discussion**

Critical adhesion energy dependence on number of thermal cycles and peak temperature.—The beam specimen configuration for the Si/SiO<sub>2</sub>/BCB/SiO<sub>2</sub>/Si samples is depicted in Fig. 4 and represents a bonded wafer stack that may well play a large role in 3D technology.<sup>5-8</sup> A double layer of BCB (1.3  $\mu$ m on each wafer, for 2.6  $\mu$ m total thickness) is sandwiched between two silicon wafers coated with 1  $\mu$ m of PECVD oxide. Figure 4 also shows the effects



Figure 6. Geometry of PECVD oxide on silicon wafer and temperature dependence of residual stress of PECVD oxide on silicon wafer during the first and second thermal cycles: (a) peak temperature of 350 and (b) 400°C.

of the number of thermal cycles and peak temperature on critical adhesion energy of this wafer stack. The measured critical adhesion energy reflects the bond between PECVD oxide and BCB, as that is the interface that failed during four-point bending. In these experiments, a substantial increase (at least 16%) in critical adhesion energy was observed after the first thermal cycle with peak temperatures of 350 and 400°C, and remains relatively unchanged after further thermal cycles. Table I summarizes critical adhesion energy results for one, five, and ten thermal cycles and three peak temperatures (350, 400, and 450°C). Based on these results, it seems that a single thermal cycle is sufficient to ensure essentially maximal mechanical stability.

The measured critical adhesion energy,  $G_{\rm c}$ , is<sup>23,24</sup>

$$G_{\rm c} = G_0 + G_{\rm residual} + G_{\rm p}$$
<sup>[4]</sup>

where  $G_0$  reflects the energy used to break bonds at the interface,  $G_p$  is a contribution due to plastic deformation, and  $G_{\text{residual}}$  is a contribution due to deformation energy by residual stresses.  $G_{\text{residual}}$  is central to our proposed explanation for the observed first cycle ef-



**Figure 7.** Geometry of BCB on silicon wafer and temperature dependence of residual stress of BCB on silicon wafer during the first and second thermal cycles: (a) peak temperature of 350 and (b) 400°C.

fect, *i.e.*, the increase in critical adhesion energy is due to an increase in  $G_{\text{residual}}$ , mostly after the first thermal cycle.  $G_{\text{p}}$  does not seem to play a role in this high-temperature thermal cycle process. If  $G_{\rm p}$  had changed during further thermal cycling, the critical adhesion energy at the relevant interface after five and ten cycles would differ from that after one cycle. This was not observed; the critical adhesion energies measured after five and ten cycles were similar to that measured after one cycle. This close tracking of the trend in critical adhesion energy with the trend in residual stress indicates a significant likelihood that the critical adhesion energy at the interface between BCB and PECVD oxide layer depends mainly on changes in G<sub>residual</sub> during thermal cycle. For the sample geometry of Fig. 4, a large decrease in the residual stress of one or both PECVD oxide layers during the first thermal cycle leads to stress relaxation at the interface between BCB and PECVD oxide layers. An increase in  $G_{\text{residual}}$  results in an increase in critical adhesion energy.

To evaluate the above explanation of the first cycle effect, *i.e.*, as due to the effects of residual stress on deformation energy ( $G_{\text{residual}}$ ) and  $G_{\text{c}}$ , stacked layers consisting of BCB and PECVD oxide films on silicon wafers were studied (Fig. 5). Figure 5 also shows the dependence of residual stresses in the stacks on the number of cycles and peak temperatures used during thermal cycles. For both

peak temperatures of 350 and 400°C, the stacked layers are in overall compressive stresses, which are released during the first thermal cycle (from -55 to -30 MPa for a peak temperature of 400°C and from -55 to -42 MPa for a peak temperature of 350°C). The stress trajectory of the stacked layers during the first thermal cycle for both peak temperatures shows plastic behavior over 300°C. It is believed that the plastic behavior of the stacked layers at temperatures over 300°C during the first thermal cycle is caused by a decrease (in magnitude) in residual stress in the PECVD oxide film due to a chemical reaction (discussed below). Unlike the first thermal cycle, little or no hysteresis was observed during the second thermal cycle, *i.e.*, residual stress was not further released, presumably because the chemical reaction in the PECVD oxide layer neared completion during the first cycle.

To further evaluate the first cycle effect, the dependences of residual stress on the number of thermal cycles and the peak temperatures used in the thermal cycles for each film (PECVD and BCB) were examined individually. We relate the stress released in the stacked layer consisting of BCB and PECVD oxide layers to the stress released in samples with PECVD or BCB layers. The force in the stacked layer consisting of BCB and PECVD oxide layers is approximated by the sum of forces from the BCB and PECVD oxide layers as

$$\sigma_{\text{total}} t_{\text{total}} \approx \sigma_{\text{oxide}} t_{\text{oxide}} + \sigma_{\text{BCB}} t_{\text{BCB}}$$
 [5]

where  $\sigma_{oxide}$  and  $\sigma_{BCB}$  are residual stresses in the oxide and BCB layer, respectively,  $\sigma_{total}$  is the residual stress of the stacked layer consisting of BCB and PECVD oxide layers,  $t_{oxide}$  and  $t_{BCB}$  are thicknesses of the oxide and BCB layer, respectively, and  $t_{total}$  is the total thickness of the stacked layer consisting of BCB and PECVD oxide layers. Stress comparisons of the stacked layer consisting of BCB and PECVD oxide to individual PECVD oxide and BCB film show that the relaxation in residual stress of PECVD oxide layer leads to the decrease in residual stress of the stacked layer and eventually, the decrease in residual stress at the interface between BCB and PECVD oxide layer.<sup>27</sup>

The geometric configuration of PECVD oxide on a silicon wafer and the temperature dependence of residual stress of the oxide layer after thermal cycles are shown in Fig. 6. The compressive stress in the PECVD oxide layer is mostly released during the first thermal cycle (from -320 to - 230 MPa for a peak temperature of 400°C and from -320 to -280 MPa for a peak temperature of  $350^{\circ}$ C). It is believed that this stress relaxation is mainly caused by the change in chemical composition by condensation reaction of silanol groups within the PECVD oxide layer (described below). The change in chemical composition leads to densification in the chemical struc-ture of the PECVD oxide layer.<sup>26,27</sup> The condensation reaction is almost completed during the first cycle, leading to small hysteresis in residual stress during the second cycle and subsequent cycles. From Fig. 5 and 6, the magnitude of stress released at 400°C peak temperature is larger than that released at 350°C peak temperature. This may be because the extent of chemical reaction in the oxide layer increases as the peak temperature increases.

Figure 7 shows the residual stress during the first and second thermal cycles for peak temperatures of 350 and 400°C for the BCB-on-silicon configuration shown. BCB that is cured using the same thermal process as in our baseline BCB bonding process is in tensile stress during the postcuring thermal cycles. During the first heating cycle, BCB becomes plastic above  $\sim 300^{\circ}$ C and the stress is relaxed.<sup>29</sup> At temperatures above 300°C, BCB may be further cured because  $\sim 12\%$  of the BCB precursors are not cured during the baseline thermal cycle. As a result of this additional cure, the residual tensile stress is reset to near zero at the glass transition temperature corresponding to the increased BCB cure and then increases during the cooling process. During the second and subsequent thermal cycling, changes in the residual stress are small, indicating that the BCB has stabilized and further curing has slowed appreciably. Because the magnitude of residual stress change in BCB (tensile stress) is smaller than that in PECVD oxide (compres-



Figure 8. Percentage cure dependence of glass transition temperature (adapted from Dow Chemical, Inc.).  $^{35}$ 

sive stress), the change in residual stress (stress relaxation) at the interface between BCB and PECVD oxide layers is dominated by changes in the PECVD oxide layer. It is reassuring that the stress values shown in Fig. 5-7 are reasonably consistent with Eq. 5.

Additionally, adhesive failure occurred, during four-point bending tests, at the interface between BCB and PECVD oxide layers for thermal cycling tests performed with peak temperatures of 350 and 400°C. For thermal cycles with a peak temperature of 450°C, critical adhesion energies are very low (less than 0.5 J/m<sup>2</sup>) irrespective of the number of cycles, and cohesive failure occurred within the BCB layer during four-point bending tests. Clearly, 450°C is beyond the acceptable range for thermal cycling of BCB, as previously reported.<sup>19,32</sup>

Effect of thermal cycling on BCB thermal stability.-Liquid-like BCB resin may be considered to be in the near-zero stress state until curing starts and BCB solidifies. During cooling, the solidified BCB contracts more than the adjacent PECVD oxide layer or silicon substrate due to the higher CTE. The values of CTE are ~52 ppm/°C (25-250°C) for BCB,<sup>33</sup> ~0.5 ppm/°C for PECVD SiO<sub>2</sub>,<sup>25</sup> and ~2.6 ppm/°C for silicon.<sup>34</sup> The buildup of residual stress in BCB,  $\sigma_{BCB}$ , during cooling after curing (or after any thermal excursion during processing) is primarily caused by the CTE mismatch between the glue and its adjacent layer. The magnitude of the stress depends on the difference between cure temperature and reference temperature (or between peak cycle temperature and reference temperature) and can be expressed as

$$\sigma_{\rm BCB} = \frac{E_{\rm BCB}}{1 - \nu_{\rm BCB}} (\alpha_{\rm BCB} - \alpha_{\rm substrate}) (T_{\rm process} - T_{\rm reference}) \quad [6]$$

where  $E_{\rm BCB}$  and  $\nu_{\rm BCB}$  are Young's modulus and Poisson's ratio for BCB,  $\alpha_{\rm BCB}$  and  $\alpha_{\rm substrate}$  are average CTE values for BCB and substrate over the temperature ranges of interest, and  $T_{\rm process}$ and  $T_{\rm reference}$  are the process and ambient temperature, respectively. Using 250 and 25°C for the process and reference temperatures, the previous CTE values for BCB and Si, a Young's modulus of BCB of 2.9 GPa,<sup>33</sup> and Poisson's ratio of BCB of 0.34,<sup>33</sup> an estimated value for  $\sigma_{\rm BCB}$  is 40 MPa. This is in rough agreement with the measured values (see Fig. 7).

As thermal cycling after bonding proceeds, BCB may be further stabilized because stress hysteresis between heating and cooling steps decreases and additional curing (cross-linking) occurs during the process, or BCB bonds may be broken during high-temperature thermal cycling. In either case, the glass transition temperature and the residual stress of BCB are affected. Evaluations of the effects of thermal cycling on residual stress, glass transition temperature, and cure percentage are therefore critical to establish a stabilized BCB state (thermal stability of BCB) and to delineate the key parameters needed for the increase of critical adhesion energy at the glue interface. The residual stress and glass transition temperature,  $T_g$ , can be determined by thermal cycling. Based on the estimated  $T_g$  value, the



**Figure 9.** Temperature dependence of residual stress for BCB layer on silicon wafer during multiple thermal cycle tests: (a) peak temperature of 350, (b) 400, and (c) 450°C.



**Figure 10.** Schematic diagrams showing stress state and change of chemical structure related to the condensation reaction of neighborhood silanol groups.<sup>26</sup> (a) Basic siloxane (Si-O-Si) configuration. (b) After deposition, the Si-to-Si distance is very close for the double OH inclusion, leading to compression. (c) After thermal cycling, the Si-to-Si distance is long compared to the basis Si-O-Si configuration, leading to tension.

cure percentage is estimated using a curve of  $T_g vs.$  cure percentage curve, as shown in Fig. 8.<sup>35</sup> The thermal stability of BCB is evaluated at three different temperatures (350, 400, and 450°C) by residual stress measurements. The evaluations of the BCB cure process and BCB thermal cycle tests performed with the three temperatures are summarized below.

After BCB cure.—The BCB cure process is performed using the same thermal process as the baseline BCB bonding, but without application of pressure. After the cure reaction, glass transition temperature and cure percentage are examined during subsequent thermal cycles. Figure 9 shows BCB stress as functions of temperature during multiple thermal cycles for peak temperatures of 350, 400, and 450°C. For all results, an initial residual stress of 35 MPa is observed. As the temperature increases, the residual stress decreases and becomes nearly zero at 300°C. Because the glass transition temperature is defined as the temperature at which the stress is near zero, 300°C is the glass transition temperature of the BCB after curing. As shown in Fig. 8, the corresponding cure percentage of BCB is ~88%.

Thermal cycles to a peak temperature of  $350^{\circ}$ C.—Figure 9a shows the BCB residual stress as a function of temperature during multiple thermal cycles at a peak temperature of  $350^{\circ}$ C. As thermal cycling proceeds from the first to the seventh thermal cycle, the magnitude of stress hysteresis between heating and cooling steps is reduced. We conclude that the chemical structure of bulk BCB is being stabilized by repeating the thermal cycle. At the eighth cycle, the stress hysteresis is almost zero, indicating that BCB is mostly stabilized. When the glass transition temperature induced in the stabilized state of Fig. 9a is compared with glass transition temperature *vs.* cure percentage curve of Fig. 8, the cure percentage of stabilized BCB is  $\sim$ 94%.

Thermal cycles to a peak temperature of  $400^{\circ}$ C.—Figure 9b shows the BCB residual stress *vs.* temperature during multiple thermal cycles performed to a peak temperature of  $400^{\circ}$ C. Proceeding from the first to the fourth thermal cycling, the magnitude of stress hysteresis between heating and cooling steps is reduced. From the fifth cycle, the stress hysteresis is almost zero, indicating that BCB is stabilized. When the glass transition temperature induced in the stabilized state of Fig. 9b is compared with cure percentage *vs.* glass transition temperature curve of Fig. 8, the cure percentage of stabilized BCB is more than 95%.

Thermal cycles to a peak temperature of  $450^{\circ}$ C.—Figure 9c shows the temperature dependence of stress for BCB during multiple cycles at a peak temperature of  $450^{\circ}$ C. From the second thermal cycle, the stress hysteresis between heating and cooling steps is almost zero. It is believed that BCB is damaged and becomes brittle due to excessive thermal load during this high peak temperature thermal cycling. However, the bulk structure of BCB presumably prevents complete disintegration of BCB and maintains the structure of an unstable solid state. Hence, the structure collapses even under small external impacts. The low critical adhesion energy value (<0.5 J/m<sup>2</sup>) obtained after this process is consistent with the above explanation.

In summary, thermal cycling at a peak temperature of 400°C requires a smaller number of cycles (five cycles) to reach a stabilized BCB state compared to using a 350°C peak temperature (eight cycles) and the cure percentage at the stabilized state increases (the 400°C cycling reaches more than 95% cure, while the 350°C cycling reaches  $\sim$ 94% cure). Unlike thermal cycling performed at peak temperatures of 350 and 400°C, BCB degrades appreciably during thermal cycling at a peak temperature of 450°C, presumably through the dissociation of Si-C bonds within BCB.<sup>32</sup> Cohesive failure is observed during four-point bending for this case.

#### Phenomenological Model

Using the experimental results above, a phenomenological model was developed that explains the effect of thermal cycling on critical adhesion energy and residual stress at interfaces of interest, including BCB and PECVD oxide layers. The key point of the model suggested here is to understand how the chemical reaction (condensation reaction) of the PECVD oxide layer evolves during thermal cycling. The chemical reaction leads to relaxation of residual stress in PECVD oxide layers, an increase in  $G_{\rm residual}$ , and an increase in  $G_{\rm c}$  at the interface between BCB and oxide layers.

The increased critical adhesion energy in a bonded wafer pair, which consists of two PECVD oxide-deposited silicon wafers bonded with 2.6 µm of BCB thickness, depends on the increased deformation energy due to residual stress, caused by stress relaxation of the PECVD oxide layer that occurs during the first thermal cycle. Of special interest is a large decrease in magnitude of the residual stress of PECVD oxide layer during the first cycle, from a compressive stress of -330 to -230 MPa for a peak temperature of 400°C, and from -330 to - 280 MPa for a peak temperature of 350°C (see Fig. 6), because stress relaxation of the PECVD oxide layer is mainly caused by the decrease in residual stress. The changes in residual stress of the PECVD oxide layer are related to its deposition and the thermal cycles. During deposition of the PECVD oxide layer, two chemical structures are produced.<sup>36</sup> One is the desirable siloxane (Si-O-Si) structure as shown in Eq. 1 and Fig. 10a, and the other structure is two adjacent terminating silanol (Si-OH) groups produced by incomplete oxidation of silane  $(SiH_4)$  as shown in Fig. 10b<sup>26</sup> and

$$2SiH_4 + 5N_2O \rightarrow 2SiO_{3/2}OH(s) + 3H_2 + 5N_2$$
[7]

The reaction of Eq. 7 can occur in the presence of the excess  $N_2O$  through the replacement of one of the bridging -O- atoms from  $SiO_2(s)$  with two terminating -OH groups to form two silanol bonds. The volume occupied by the -OH groups in the second structure is greater than that occupied by a bridging -O- atom, leading to compression at this site.<sup>22</sup> The formation of silanol species by Eq. 7 also means substituting the strong siloxane bonds with comparatively weak hydrogen bond interactions between two -OH groups. This decreases the structural integrity and decreases the resistance to deformation. However, at the elevated temperatures seen during thermal cycling, two such silanol species may undergo a condensation reaction, leading to the evaporation of water and the formation of a siloxane linkage as



Figure 11. FTIR absorbance spectra for PECVD oxide laver deposited on silicon wafer after deposition, after the second thermal cycle with peak temperature of 350°C, and after the second thermal cycle with peak temperature of 400°C: (a) FTIR traces over the entire wavelength range (400-4000 cm<sup>-1</sup>), (b) FTIR traces showing changes in peaks of siloxane bond, and (c) FTIR traces showing change in peak of silanol bond.

 $2SiO_{3/2}OH \rightarrow 2SiO_2(s) + H_2O$  [8]

The distance between Si and Si across this linkage is longer than that for a normal linkage, leading to tension at this stage.<sup>26</sup> Equation 8 induces a decrease in residual stress of the oxide layer, and the large compressive deposition stresses become smaller compressive stresses during thermal cycling.

The changes in chemistry of bulk PECVD oxide layers on silicon wafers during thermal cycling were studied by absorbance FTIR. The absorbance FTIR beam passes through the silicon wafer and the PECVD oxide layer, providing information about the production of siloxane bonds by the condensation reaction (Eq. 8). Figure 11a shows FTIR traces over the entire wavelength range (400 -4000 cm<sup>-1</sup>) for as-deposited PECVD oxide, PECVD oxide after the second thermal cycle with peak temperature of 350°C, and PECVD oxide after the second thermal cycle with peak temperature of 400°C. Figures 11b and c present enlarged FTIR traces showing changes in peaks of siloxane and silanol bonds, respectively. The siloxane peaks include the Si-O-Si rocking band at  $\sim$ 450 cm<sup>-1</sup>, the Si-O-Si bending band at  $\sim 805 \text{ cm}^{-1}$ , and the Si-O-Si stretching band at  $\sim 1070 \text{ cm}^{-1}$ , and the silanol peak is in 3670-3680 cm<sup>-1</sup>. After thermal cycling, the Si-O-Si peaks increase, the Si-O-Si stretching band shifts to a higher wave number, and the silanol peak decreases, indicating that condensation reaction occurs during the thermal cycling. These results are consistent with the observed temperature dependence of residual stress in the PECVD oxide layer after thermal cycling (see Fig. 6).

The proposed mechanism results in: (*i*) an increase of the deformation energy due to residual stress,  $G_{\text{residual}}$ , and (*ii*) an increase in critical adhesion energy,  $G_{\text{c}}$ , through the reduction of large compres-

sive deposition stresses in the PECVD oxide layers during thermal cycling.

### Conclusions

Some effects of thermal cycling on critical adhesion energy and residual stress for bonded BCB-bonded PECVD oxide-coated wafers were examined quantitatively. In thermal cycling tests performed to evaluate the bonding interface between BCB and PECVD oxide-coated wafers, relaxation of residual stress in the PECVD oxide layer that occurs during the first thermal cycle dominates the increase in critical adhesion energy. After the first thermal cycle, the critical adhesion energy increases relatively slightly, presumably because the change in residual stress in the PECVD oxide layer nears completion during the first cycle. The magnitudes of residual stress release and critical adhesion energy increase in the 400°C thermal cycle process are larger than those observed in the 350°C process.

We believe that differences in the extent of chemical reaction in the oxide layer as the peak temperature changes, analyzed by FTIR, lead to the differences in critical adhesion energies and residual stresses between the 350 and 400°C processes. The siloxane bonds formed by the condensation reaction in the PECVD oxide layer trigger the relaxation of residual stress. The condensation reaction and its relationship to relaxation of residual stress in PECVD oxide layers were supported by following the change in chemistry within the PECVD oxide layer by FTIR.

Thermal cycling tests to evaluate BCB thermal stability were performed at 350, 400, and 450°C peak temperatures. When the peak cycle temperature is 350°C, BCB reaches steady state at the eighth thermal cycle, and percentage cure at the steady state is ~94%. When the peak cycle temperature is 400°C, BCB reaches steady state at the fifth thermal cycle, and percentage cure at the steady state is more than 95%. Thermal cycling performed at a peak temperature of 450°C gives rise to cohesive failure within the BCB layer with very low critical adhesion energy (<0.5 J/m<sup>2</sup>).

The results presented improve our understanding of the thermal and mechanical stability of BCB-bonded wafer stacks. In turn, this can help us establish a process window to maintain stable BCB layers without degrading previously deposited BCB layers. The phenomenological model described suggests that the chemical reaction within the PECVD oxide layer leads to the relaxation of residual stress in the oxide layer and increases the critical adhesion energy at the interface between BCB and oxide layer during thermal cycling.

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