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Indirect Wafer Bonding and Epitaxial Transfer of GaSb-Based Materials

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Results from a study of indirect wafer bonding and epitaxial transfer of GaSb-based materials are presented. Benzocyclobutene (BCB) was used as a bonding agent to bond GaSb and epitaxial structures lattice matched to GaSb onto Si, GaAs, and sapphire carrier substrates. To better understand sources of stress during the bonding process, which can result in cracking and subsurface damage of the GaSb-based materials, BCB's hardness and reduced elastic modulus were measured at various stages during the curing process. Based on the results of curing experiments, a bonding and epitaxial transfer process for GaSb-based materials was then developed. Following bonding, using an experimentally determined low-stress cure cycle, GaSb substrates were removed from epitaxial layers of InAsSb using a combination of mechanical thinning and polishing followed by selective chemical etching using a hydrofluoric and chromic acid solution. Etch selectivity data are also presented where selectivity greater than 100:1 is achieved for GaSb:InAsSb.

Key words: Wafer bonding, GaSb, BCB, InAsSb, selective etch, mechanical properties

INTRODUCTION

Organic polymers have found use in semiconductor fabrication due to their desirable thermal, mechanical, and electrical properties. In particular, benzocyclobutene (BCB) from Dow Chemical Co., commercialized under the name Cyclotene®, has been used extensively in microelectronic and optoelectronic fabrication. A low dielectric constant, strong adhesion, low moisture absorption, and planarization properties have allowed BCB to be used for a variety of applications. These include optical waveguides,[1,2] interlayer dielectrics in the fabrication of interconnects for multichip modules,[3,4] sidewall passivant for mesa photodiodes,[5] and as an adhesive for indirect wafer and die bonding.[6,7] For wafer and die bonding, BCB provides a new scheme for hybridization of III–V detector arrays and silicon readout integrated circuits (ROICs). This hybrid integration is advantageous because it allows for separate optimization of the detector arrays and Si-based readout electronics. Typically, detector and readout circuit integration is accomplished using indium bump bonding technology. The drawbacks of this methodology are that standard indium bump widths limit detector pitch and alignment accuracy is limited by the reflow of the indium bumps. The use of BCB for wafer and die bonding allows for decreased detector pitch and finer alignment tolerances compared with conventional indium bump bonding.

With the realization of III–V devices lattice matched to GaSb, indirect wafer bonding using BCB was examined as a possible low-stress method for wafer hybridization and epitaxial transfer. GaSb-based devices that can benefit from epitaxial transfer include back-illuminated focal-plane arrays and thermophotovoltaic cells. In both cases, flipping and bonding allows for thinning or removal of the GaSb substrate, which reduces free carrier absorption, increasing device performance. With several device and packaging schemes in mind, experiments were carried out aimed at bonding GaSb epitaxial wafers to one of three carrier substrates: Si, GaAs, and sapphire.

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EXPERIMENTAL PROCEDURES

A bonding procedure using BCB has been shown to work well with Si onto Si. In this process a 2-μm-thick BCB layer is spin-coated onto the target and carrier wafers and the two are soft-baked on a hot-plate at 100°C for 15 min. The samples are then mounted face to face and placed in a vacuum chamber. A modest amount of pressure is applied ($\sim$2 kg/cm^2), and the samples are heated to 350°C. Following bonding, it was possible to mechanically thin one of the Si pieces to 100 μm.

During initial attempts to hybridize GaSb samples onto various substrates using the Si BCB bonding processes previously described, the GaSb was prone to cracking during the bonding process or during the mechanical thinning and polishing process. Once a fracture had formed, it often propagated through the entire hybridized structure. The source of the fracturing is suspected to be a result of induced stress that results from the bonding of two materials with varying amounts of wafer bow and differences in thermal expansion coefficients at elevated temperatures. As the bonded structure cools, each component relaxes to a different length, which in turn generates stress.

Alleviation of the fracturing problems requires relieving the stress induced during the bonding process. This requires an understanding of the evolution of the mechanical properties of BCB throughout the curing process. Understanding of the mechanical properties of the BCB may also aid in addressing potential issues during postfabrication packaging. To that end, a study of BCB's elastic modulus and hardness as a function of curing percentage was carried out, culminating in a successful wafer bonding process. This, in turn, allowed for the development of a selective etch process in which a thinned GaSb substrate could be completely removed from epitaxial InAsSb using a selective etch consisting of hydrofluoric and chromic acid.

Three sets of experiments were performed in order to arrive at a repeatable and mechanically reliable epitaxial transfer process. First, the reduced elastic modulus and hardness of BCB as a function of curing percentage were determined using a combination of Fourier-transform infrared spectroscopy and nanoindentation. Next, bonding experiments were carried out, in which GaSb substrates were bonded to Si, GaAs, and sapphire substrates at varying bonding temperatures. Finally, etch selectivity experiments were performed in which the etch rates of various hydrofluoric and chromic acid solutions were measured for both InAsSb and GaSb, resulting in a selective etch in which GaSb could be removed from a thin InAsSb etch-stop layer.

Benzocyclobutene Curing Properties

For the determination of the BCB curing percentage as a function of temperature and time, samples of BCB were prepared by spinning $\sim$5-μm layers of Cyclotene 4026 onto one side of $\sim$4-cm^2 double-side-polished Si substrates. The backsides of the samples were then cleaned using acetone, methanol, and isopropynol in order to remove any BCB that may have unintentionally accumulated there during spin-coating. The samples were then cured in a glass tube furnace for either 10 min or 20 min. The curing was performed at temperatures ranging from 160°C to 300°C in inert nitrogen atmosphere with the temperature monitored using a thermocouple placed directly below the sample in contact with the sample mount. Following curing, the samples were cleaved in half. One half of the sample was used for curing measurements, while the other was used to measure BCB's hardness and reduced elastic modulus.

The curing percentage of each sample was determined by examining the spectra of the BCB-coated samples (Fig. 1) using Fourier-transform infrared (FTIR) transmission spectroscopy. Measurements were made at room temperature using a Nicolet 760 FTIR spectrometer. The curing percentage was calculated from the FTIR data using the following formula:[8]

$$\%_{\text{cure}} = 95\frac{(A_{1500}/A_{1255})}{(A_{1500}/A_{1255})_{\text{full}}}, \quad (1)$$

where A_{1255} and A_{1500} are the absorbance peak heights at 1255 cm^{-1} and 1500 cm^{-1}, respectively. $(A_{1500}/A_{1255})_{\text{full}}$ denotes a fully cured sample. The decrease in absorbance of the 1475 cm^{-1} peak is associated with the vibration of the four-membered cyclobutene group, while the increase in the 1500 cm^{-1} peak is indicative of the formation of a trisubstituted teterahydronaphthalene group as a result of curing. The peak at 1255 cm^{-1} is unaffected by polymerization and is used to normalize the response curves. Because oxidation has a dele-

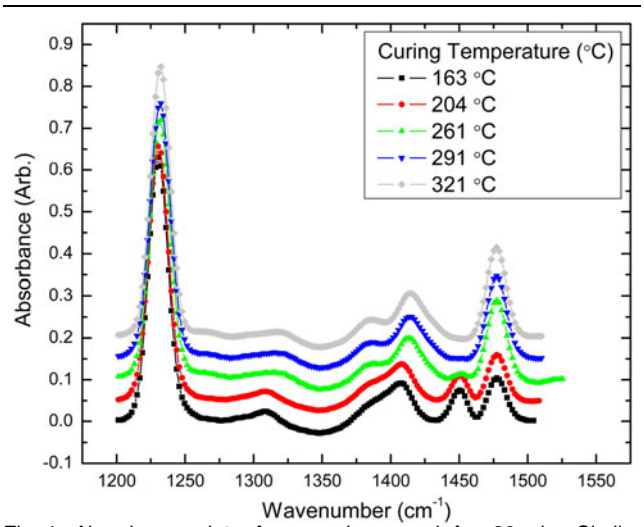

Fig. 1. Absorbance data for samples cured for 20 min. Similar results were obtained for data taken with a 10 min curing cycle.

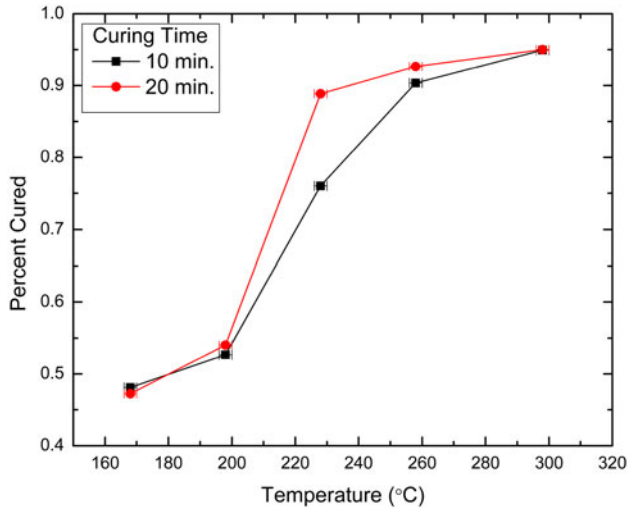

Fig. 2. BCB curing percentage as a function of temperature.

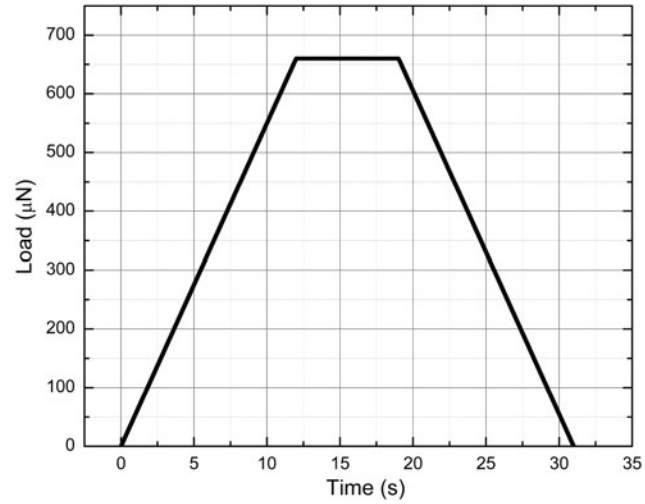

Fig. 3. Trapezoidal loading function used for nanoindentation measurements.

terious effect on peak height analysis, the absorbance at 1700 cm^{-1} and 1775 cm^{-1} was examined. The absence of peaks at these values indicated that the samples had not oxidized and that the curing measurements were valid. Curing percentage as a function of time and temperature is shown in Fig. 2. For all measurements, background data taken on bare Si wafers were subtracted out. For the peaks of interest, baseline fitting was performed as outlined in Ref. 8.

Mechanical Properties of Benzocyclobutene

Measurements of the reduced modulus and hardness of the partially cured BCB were made using a Hysitron Ubi 1 nanomechanical analyzer. Arrays (3 × 3) of indents were made using a Berkovich tip, with each indentation spot 200 μm away from adjacent indents. Using a trapezoidal load function (Fig. 3), a starting load of 600 μN was used for all measurements, while the ending loads were varied to ensure that the indentation depth did not exceeded 10% of the BCB layer thickness (Fig. 4). From the load versus displacement curves, the reduced modulus and hardness values were determined. The hardness, H, of the partially cured BCB is given by

$$H = \frac{P_{\max}}{A}, \tag{2}$$

where $P_{\max}$ is the maximum applied force and A is the projected contact area. The reduced modulus, E_r, is given by

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A(h_c)}} S, \tag{3}$$

where S is determined from dP/dh (Fig. 4) and h_c is the contact depth.

From the hardness versus curing data (Fig. 5), it was found that the mechanical properties of the BCB change rather abruptly near 90% cure. This indicates that slow temperature ramping during the bonding process is needed to achieve low-stress bonds. While oxidation affects the ability to measure curing percentage, hardness and elastic modulus data taken on oxidized samples (samples not cured in a nitrogen environment) yielded the same results as samples cured under identical time and temperature conditions in a nitrogen environment. This indicates that oxidation does not have a significant effect on the mechanical properties of cured BCB. An Arrhenius plot of the curing percentage as a function of temperature allowed the activation energy of the opening of the benzocyclobutene ring to be calculated. A value of 39.1 kcal/mol was found, in relatively good agreement with the value of 38.2 kcal/mol reported by Hahn et al.[9] As with Hahn et al., first-order kinematics was assumed.

Indirect Wafer Bonding and Mechanical Thinning

Following the curing and hardness measurements, a series of bonding experiments were carried out in which 4-cm^2 GaSb pieces were bonded to either Si, GaAs or sapphire pieces with areas slightly larger than 4 cm^2. Based on the hardness and reduced modulus data, the temperature ramping profile during the bonding process was set so that 75 min elapsed from the beginning of the bond to when the maximum temperature was reached (Fig. 6). Using this new bonding recipe, bonds were made in which the maximum bonding temperature was varied from 180°C to 300°C in 20°C increments. Following bonding, the GaSb substrates were mechanically thinned using a Logitech PM2A lapping machine with 3-μm Al_2O_3 grit down to thickness of 100 μm. All samples bonded at 260°C or

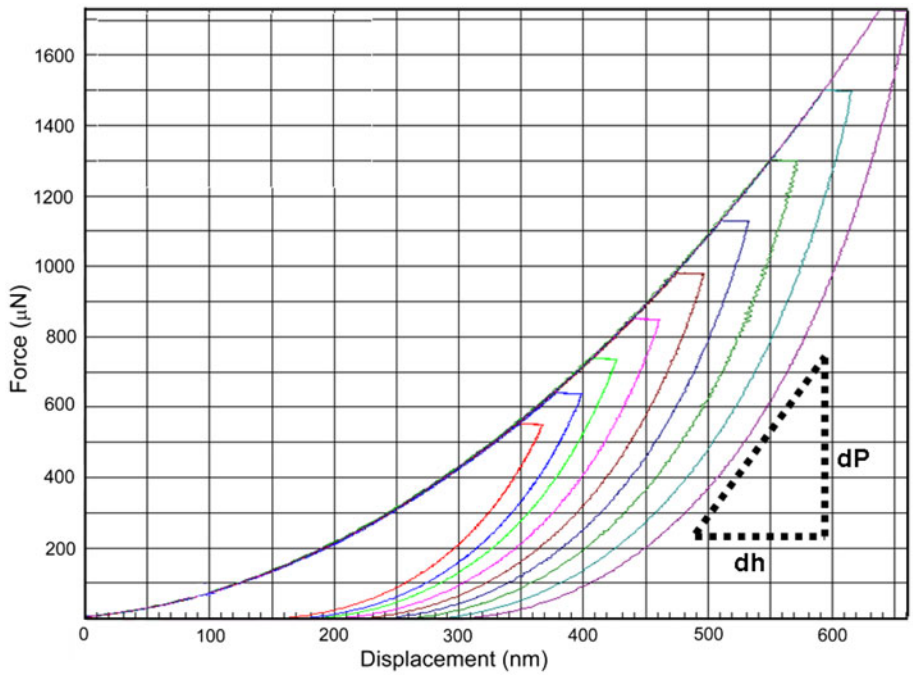

Fig. 4. Force versus displacement for different starting loads.

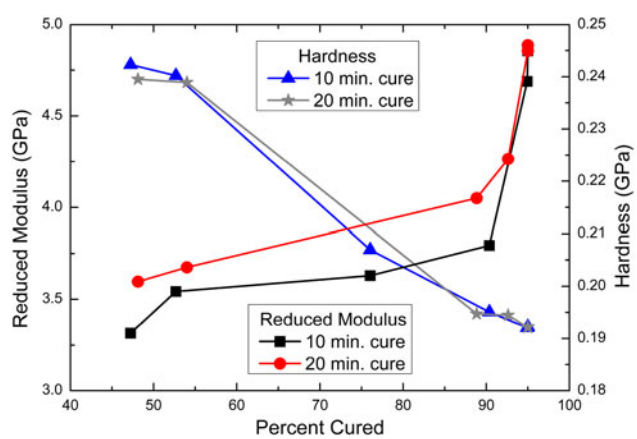

Fig. 5. BCB hardness and reduced elastic modulus versus curing percentage.

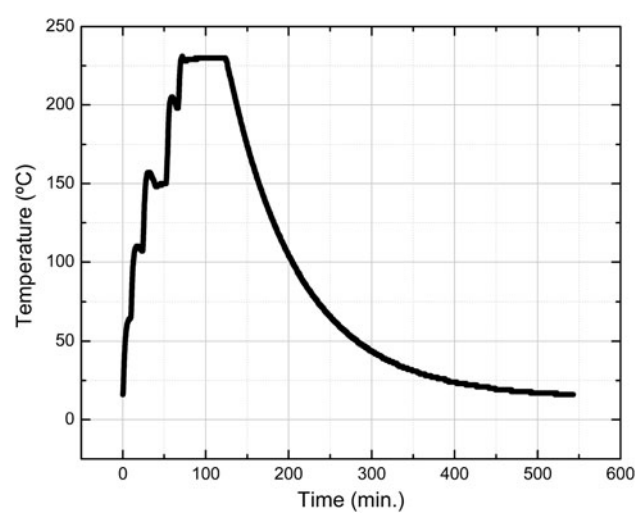

Fig. 6. Typical BCB bonding temperature profile.

below were successfully thinned without delamination or visible fracturing. The reliability and repeatability of the bonding and substrate thinning process was verified by many successful bonds in which GaSb was bonded to sapphire and mechanically thinned to 50 μm.

GaSb and InAsSb Etch Selectivity

A final set of experiments were performed to determine the relative concentrations of HF and CrO_3 that result in a high degree of selectivity between InAsSb and GaSb. Etch experiments were performed on both n-type GaSb wafers and undoped epitaxial InAsSb grown on GaSb substrates. For the etch experiments, Ti/Au was deposited and patterned for use as an etch mask. The samples were etched for 3 min and then rinsed with deionized water and dried with N_2. The etch depth was measured using a Tencor P15 profilometer. From these experiments, it was found that a solution of 1 M CrO_3 and HF (8:1) results in an etch rate for GaSb more than 100 times that of InAsSb. A contour plot of the experimental data is shown in Fig. 7.

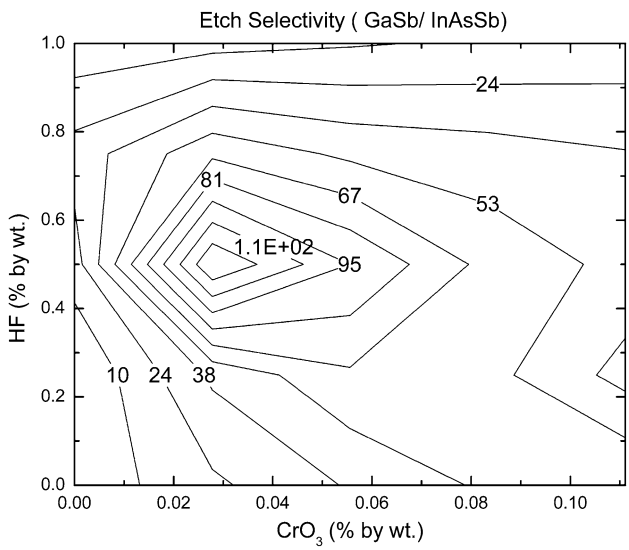

Fig. 7. Etch selectivity as a function of % weight for HF, anhydrous CrO_3, and H_2O.

CONCLUSIONS

With both a successful bonding process and selective etch developed, a full epitaxial transfer process was developed for transferring epitaxial layers grown on GaSb substrates onto sapphire. A GaSb substrate with a 1-μm-thick epitaxial InAsSb layer was cleaved into 4-cm^2 pieces. The pieces were bonded using the BCB process previously described. Following bonding, the GaSb was thinned to 50 μm using 3-μm Al_2O_3 grit. The substrate was then polished to $\sim$20 μm using a solution of 97% colloidal silica polishing slurry and 3% sodium hypochlorite. The final 20 μm of the GaSb substrate were removed using the 1 M CrO_3 and HF (8:1) etch, stopping on the InAsSb layer. The epitaxial transfer process was shown to be highly reproducible and capable of withstanding further processing including contact lithography and etching in citric acid solutions.

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