Elastic Recoil Detection of Depletion Layer Formation During Anodic Bonding

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Abstract. Conventional elastic recoil detection (ERD) techniques have been employed in an attempt to elucidate the effects time, temperature and alkali ion content have on depletion layer formation during anodic bonding. Hydrogen and/or lithium ion concentration profiles were evaluated for both untreated and lithium-treated sodium borosilicate glass. From in situ ERD, depletion layer formation is highly dependent on temperature and alkali ion content. Lithium-treated sodium borosilicate glass improves depletion layer formation at low temperatures and at high temperatures increased ion mobility results in rapid depletion layer formation.

INTRODUCTION

Microelectro-mechanical sensor (MEMS) devices broadly define an entire array of either actuators or sensors with submillimeter moving parts, channels and/or electronics integrated within a hermetically sealed package [1,2]. Mechanically strong hermetic seals are required in order to protect the device from premature failure due to interactions with corrosive environments, externally applied mechanical stresses, and fluctuations in internal pressure. As a result, the device is able to sense different magnitudes of the same stimuli without compromising the original response characteristics to which the integrated circuitry was normalized.

Micromachining and packaging are the two main processes used for the fabrication of MEMS devices [3,4]. Micromachining refers to the development of three-dimensional structures with the use of deposition and etching techniques. Whereas micromachining processes, such as anisotropic etching are well characterized, packaging of micromachined silicon to either silicon or glass substrates is by far the most critical and expensive step of the two processes. In an effort to reduce packaging costs, a considerable amount of research is dedicated to the development of new low temperature bonding methods or modifications to existing techniques [5-7]. Bonding techniques that can be used at low temperatures without compromising bond reliability are necessary in order to minimize thermal stresses in the packaged device due to a coefficient of thermal expansion (CTE) mismatch between glass and silicon. Furthermore, lower bonding temperatures reduce compatibility requirements on other materials that may be integrated into the MEMS device, such as polymers or metal layers.

ANODIC BONDING

Common bonding techniques for MEMS are silicon fusion bonding [8-10], frit glass bonding [11], eutectic bonding [5,7,12], adhesive bonding [10] and anodic (field-assisted) bonding [4-7,13-15]. Of these bonding methods, anodic bonding is a relatively low-temperature electrochemical process used to encapsulate MEMS devices into hermetically sealed packages. For this process, a voltage of 200-2000VDC is applied across a silicon substrate and a glass cover at temperatures below the softening point of the glass [15]. Ideally, the bonding temperature is

TABLE 1. Composition of Sodium Borosilicate Glass.

Oxide	Weight Percent
SiO_2	80.6
B_2O_3	13.0
Na_2O	4.0
Al_2O_3	2.3
Trace Impurities	0.1

kept as low as possible to minimize thermal stresses due to CTE mismatch. In many cases, sodium borosilicate glass (Pyrex® Corning Glass Code 7740) is used as the glass cover, because of its similar CTE to that of silicon, insulating properties, commercial availability, low cost and bonding ease [16]. The nominal chemical composition of sodium borosilicate glass is given in Table 1. For a sodium borosilicate glass to silicon bond, CTE mismatch results in the formation of thermal residual stresses strong enough to bow the packaged device during cooling from bonding temperatures above 280°C [17]. However, because of concerns with reliability and bonding kinetics, temperatures between 350-450°C are typically used to commercially bond sodium borosilicate glass to silicon.

Because simultaneous measurement of ion movement and interfacial reactions is cumbersome, the exact mechanisms responsible for the formation of an anodic bond between glass and silicon have yet to be thoroughly characterized. However, with the combination of pioneering polarization studies by Carlson *et al* [18-20] and the early anodic bonding work by Wallis [21], it is generally assumed that oxidation of the silicon (metal) anode is the primary mechanism responsible for generating bonds. During bonding, the glass cover is biased negatively with respect to the silicon substrate. Initially, the majority of the applied voltage is sustained across the thin air gap (~ 1mm) separating the two materials. The high electric field within the air gap generates electrostatic forces strong enough to pull the oppositely charged surfaces into physical contact. Physical contact is necessary for interfacial anodic oxidation to proceed. During this time, sodium ions diffuse from the region nearest the anode towards the cathode. The glass region adjacent to the anode that exhibits a substantial reduction in sodium concentration as compared to the bulk glass is referred to as the depletion layer. The diffused sodium ions are neutralized at the cathode according to the following half-reaction: $Na^+ + e^- = Na^0$. Once the two surfaces are in physical contact (electrostatically bonded) and sodium ions have been displaced from the anode, the majority of the applied voltage is isolated across the depletion layer, and a very high electric field persists. The depletion region has a relatively high resistivity and is relatively thin

with respect to the thickness of the bulk glass. The high electric field in combination with the elevated temperature is the driving force needed to diffuse the relatively immobile nonbridging oxygen ions away from the depletion region to the anode, at which point, they react with silicon forming a SiO_2 interface [21-23].

Depletion layer formation is a prerequisite for anodic bond formation; otherwise, the flux of oxygen ions required to initiate bonding is not transferred to the anode. For example, at low temperatures, when the mobility of alkali ions such as sodium is reduced and depletion layer formation is retarded a bond may not form even after several hours of electrolysis. In this situation the voltage is sustained across the width of the entire glass sample generating a low electric field. To compensate for the lack of ionic mobility and low electric field, the applied voltage can be increased depending on the voltage sensitivity of the structures that are to be encapsulated. Furthermore, care must be taken because voltage increase is limited by the dielectric strength of the glass.

ELASTIC RECOIL DETECTION

The detection of near-surface ion movement during bonding conditions may impart further insights into the dynamics of depletion layer development and thus the formation of anodic bonds. With this knowledge, bonding parameters as well as glass composition may be adjusted to achieve lower temperature bonds. In situ elastic recoil detection (ERD) [24] has been employed to determine the effect bonding time, temperature and alkali content have on depletion layer formation. ERD is an ion scattering technique that can be used to acquire concentration profiles of light elements (H → F) in the near-surface region of solids. ERD provides good depth resolution (100-250 Å) and sensitivity (~ 0.1 at. %). Unlike other ion/electron beam analysis techniques, such as secondary ion mass spectrometry and Auger electron spectrometry, where low-energy ions or electrons sputter the target surface to determine a depth profile, ERD is nondestructive and because it does not depend upon differential surface sputtering rates, the accuracy of the profile is superior.

To improve low temperature depletion layer development, sodium borosilicate glass was doped with lithium ions using ion exchange techniques. The exchange of lithium-for-sodium ions in sodium borosilicate glass has resulted in a reduction of the anodic bonding temperature to 200ºC [25,26]. In

addition to examining the role of lithium, the effect hydrogen ions have on the progression of depletion layer formation for untreated and lithium-treated sodium borosilicate glass was considered with the assistance of ERD measurements. This is of interest because in a recent study, Nitzsche *et al* [27], suggested that hydroxides in Tempax Schott #8330 (similar to Pyrex #7740) move toward the anode during bonding and react with silicon producing an oxide. These liberated, positively charged hydrogen ions then move towards the cathode, but only within the depletion layer, and pile up at the edge of the depletion region.

EXPERIMENTAL

A thin film of silicon (approximately 500 Å thick) was sputtered onto the anode side of the glass samples. The film acts as the anode and is thin enough to permit adequate near-surface analysis of the glass during bonding. A thin film is used instead of bulk silicon because of the analyzable depth limitations of ERD. A sample holder was modified so that in situ ERD analysis of anodically bonded samples could be performed. In situ ERD analysis is contingent upon the ability to heat and apply a voltage across the sample while the target chamber is under vacuum. Heating was accomplished utilizing isolated feedthroughs in which an Inconel resistive element was biased. To restrict the emission of electrons from the heating element (which can damage the detector) during bias, the Inconel element was prepackaged within ceramic insulating fiber and contained within a metal shell. The metal shell was brazed to the bottom of the target stage to ensure an adequate thermal pathway to the sample. For the voltage source, leads were attached to the bottom and top of the glass. The negatively biased lead was connected to the bottom of the stage in which the sample was seated while the positively biased lead was sandwiched between the top of the glass and a supporting clamp. The temperature was monitored on both the anode and cathode side of the glass prior, during, and after bonding runs using a Keithley 871 Digital Thermometer and an Omega HH-25KC Digital Thermometer. The drift current was monitored using an Omega HHM57A handheld digital multimeter.

ERD analysis was performed utilizing an EN tandem Van de Graaff accelerator. 16 MeV Si^{3+} ions were accelerated towards the sample at an incidence angle of 15° with respect to the sample surface. Depending on the sample (untreated or lithium treated), either hydrogen or hydrogen and lithium ions

were detected. A silicon surface barrier detector was placed behind a 12 μm Mylar filter in the path of the recoiled ions and the detected signal was sent to standard MCA electronics to generate a spectrum. The chamber was under vacuum, on the order of 5 x 10^{-7} to 5 x 10^{-6} Torr, during ion beam analysis. Beam current was measured before and after each analysis.

RESULTS AND DISCUSSION

During electrolysis, the temperature on both the anode and cathode side of the glass was recorded. It was observed that, prior to electrolysis, a temperature gradient existed across the samples and varied between 35 and 65°C. The temperature gradient varied for each sample and is believed to be due to differences in thermocouple contact. During electrolysis, an increase in temperature was recorded for both the anode and cathode side of the glass. While the sample was biased, the temperature of the anode side of the glass increased rapidly by 25-75°C, whereas, at the cathode side of the glass the temperature increased slowly by 5-20°C. The increase in temperature is believed to be the result of Joule heating effects and is more significant at the anode side than at the cathode. The significant temperature increase may be the result of ionic transport away from the anode. These observations suggest that Joule heating effects should not be ignored during anodic bonding at low temperatures. Further investigation is needed to characterize the effects of Joule heating on bond formation.

ERD has been used to systematically investigate the effect hydrogen and lithium ions, temperature and bonding time have on the formation of the depletion layer. As such, Fig. 1 shows hydrogen depth profiles of untreated sodium borosilicate glass that has been intermittently biased at 1000VDC at a temperature of 200°C as a function of time. Prior to electrolysis, at time zero, a reference hydrogen profile was measured to subsequently evaluate the progression of hydrogen after each time interval. The time interval refers to the total elapsed time the sample has been electrolyzed starting from zero.

All samples, untreated or treated, exhibited a near surface hydrogen peak; for example, refer to Fig. 1. This peak is common to glasses and, in this case, is most likely the result of moisture adsorption, dissociation, and hydrogen exchange with alkali ions inherent to the glass. However, because of ion beam interaction effects, the surface hydrogen peak
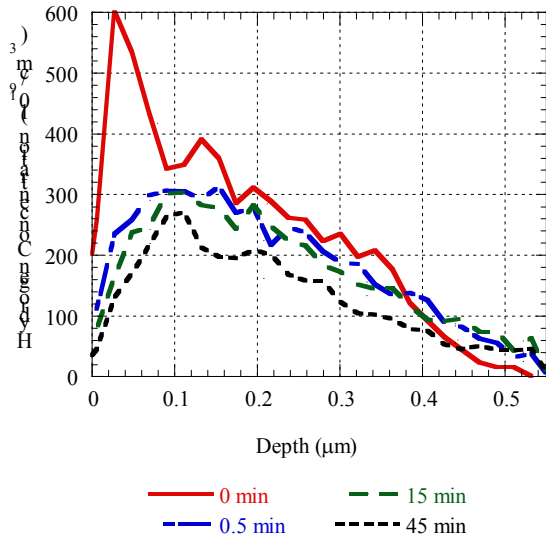
FIGURE 1. Hydrogen depth profile for untreated sodium borosilicate glass heated at 200°C and biased at 1000VDC.

significantly decreased from approximately 600 to 300 x 10^{19} hydrogen ions/cm^3 after the first analysis. Because of the energy being transferred to the surface of the specimens by the 16 MeV Si^{3+} beam, near-surface hydrogen is driven further below the surface and/or liberated as gaseous H$_2$ due to sputtering processes. A decrease of approximately half of the original hydrogen peak is observed for all samples exposed to the 16 MeV Si^{3+} beam.

As shown in Fig. 1, very little hydrogen transport occurred after the reference hydrogen profile was measured. The difference between 0.5 and 45 minute analyses indicates only a slight decrease in peak concentration. This suggests that a sodium depletion layer did not develop. This is assumed, based on a study by Nitzsche *et al* [27], in which it was determined that hydrogen is highly mobile within the alkali ion depletion layer and tends to pile up within the inside edge of this region. Consequently, the lack of hydrogen movement at 200°C, with an applied voltage of 1000VDC, suggests that the mobility of sodium is negligible and a depletion layer did not form.

Hydrogen and lithium profiles were measured in lithium-treated sodium borosilicate glass samples (Fig. 2) that were exposed to an applied voltage of 1000VDC at 200ºC. Unlike the profiles for untreated sodium borosilicate glass (Fig. 1), there is significant hydrogen movement. After 5 min the hydrogen peak has progressed from 0.04 to 0.14 µm. Correspondingly, the lithium profile (Fig. 2b) shifted from approximately 0.075 to 0.20 µm as measured from the edge of lithium peaks. Unfortunately, for these experiments, the analyzable depth range of lithium is only to 0.22 µm as a result of its higher stopping power than hydrogen. Therefore, the original depth of lithium ion exchange cannot be resolved nor the depletion layer depth after 5 min. However, consistent with previous observations [27], hydrogen ions appear to accumulate at the edge of the lithium depletion layer (or alkali ion depletion layer) during electrolysis. From Fig. 2a, the movement of hydrogen towards the cathode can most likely be correlated with the edge of the depletion layer. Therefore, after 10 min, the lithium depletion layer is estimated to be on
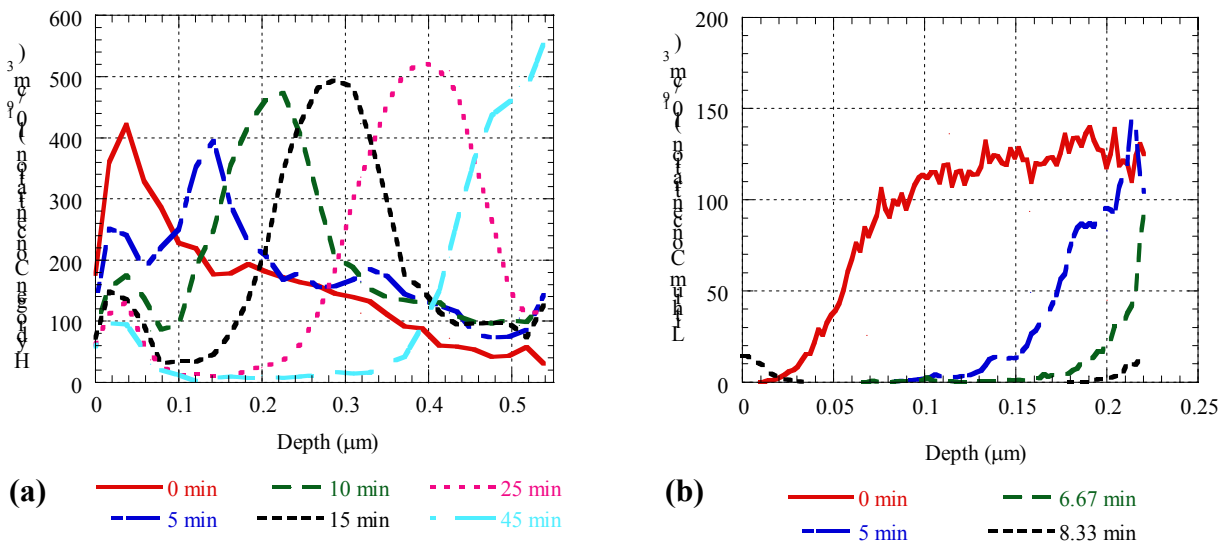

FIGURE 2. (a) Hydrogen and (b) lithium depth profiles for lithium-exchanged sodium borosilicate glass heated at 200°C and biased at 1000VDC.
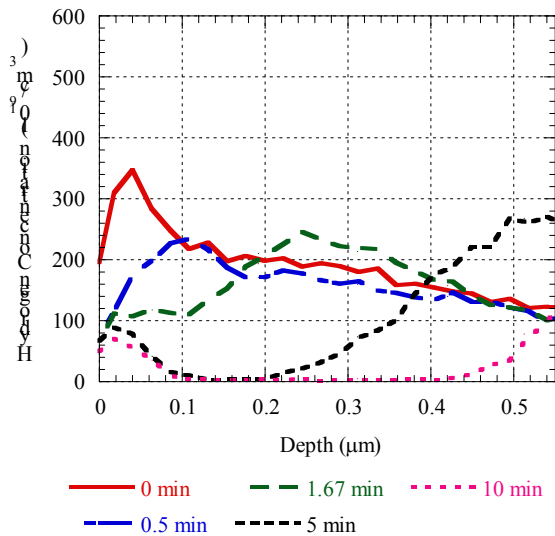
FIGURE 3. Hydrogen depth profile for untreated sodium borosilicate glass heated and biased at 250°C and 1000VDC.

the order of 0.25 μm and after 25 min, the lithium depletion layer is approximately 0.45 μm. At 45 min of electrolysis, the hydrogen peak is approximately 0.55 μm in depth, indicating a lithium depletion depth of at least 0.55 μm.

To determine the effect of temperature on depletion layer formation, untreated and lithium-treated sodium borosilicate glass were electrolyzed at 250°C with an applied voltage of 1000VDC. As shown in Fig. 3, the mobility of hydrogen ions is considerably greater compared to untreated and lithium-treated sodium borosilicate glass exposed to temperatures of 200ºC
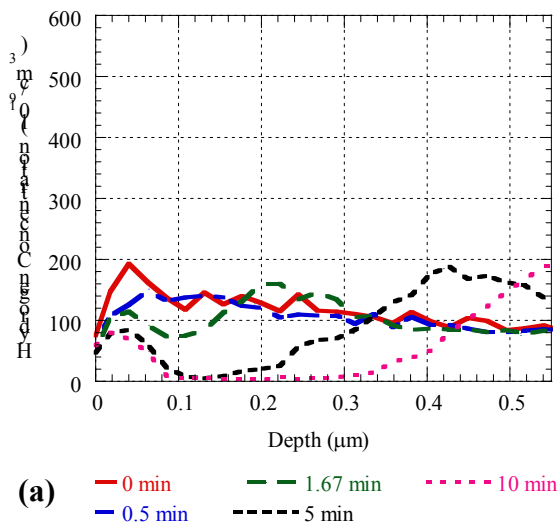
(Figs. 1 & 2a). After being electrolyzed for 10 min, the majority of the hydrogen ions have been displaced from the near-surface region of the glass to at least 0.55 μm. It appears that sodium mobility increased significantly from 200 to 250ºC. This increased sodium mobility results in rapid depletion layer formation and growth.

Hydrogen and lithium ion concentration profiles were measured for lithium-treated sodium borosilicate glass samples (Fig. 4). As with untreated sodium borosilicate at 250ºC, the hydrogen mobility is significantly greater than the samples analyzed at 200ºC. The peak hydrogen concentration after only 10 min of bias is approximately 0.55 μm below the glass surface. As expected, the mobility of lithium ions is greater at 250ºC than at 200ºC. After 5 min the lithium depletion layer was at least greater than 0.22 μm (Fig. 4b), whereas, 8.33 min were required at 200ºC in order for the lithium depletion layer to extend past 0.22 μm (Fig. 2b). Higher temperatures allow more ionic diffusion as indicated by changes in the shape of the concentration profiles. At 200ºC, the front edges of the hydrogen and lithium ion profiles are steep while at 250ºC the increase in concentration is gradual and the peaks are broadened. This difference in the distribution of hydrogen ions is observed by comparing Figures 2a and 4a and for lithium ions by comparing Figures 2b and 4b. During electrolysis at 250°C a relatively low and graded electric field exists within the depletion region; whereas, at 200°C for lithium-exchanged sodium borosilicate glass, the depletion region is thin and well-defined resulting in a higher electric field that is
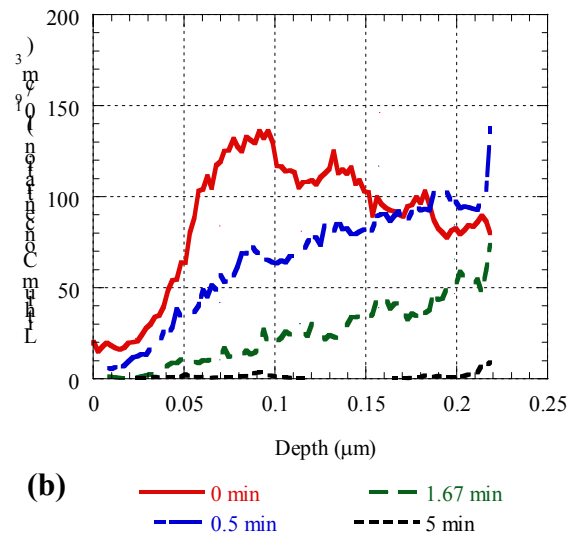
FIGURE 4. **(a)** Hydrogen and **(b)** lithium depth profiles for lithium-exchanged sodium borosilicate glass heated and biased at 250°C and 1000VDC.

uniform throughout the depletion region. The higher electric field within the depletion layer should promote oxygen ion diffusion toward the anode, thus generating lower temperature anodic bonds with silicon than what is possible using untreated sodium borosilicate glass.

Anodic bonding of bulk sodium borosilicate glass to bulk silicon at 200 and 250°C has not been reported in the literature, but it has been alluded to as being kinetically impractical. The benefits of bonding at elevated temperatures (350-450°C) are increased bonding reliability; for instance, at low temperatures electrostatic bonds may form rather than anodic bonds resulting in a significant decrease in strength and hermiticity. Also, at higher temperatures (350 to 450°C) the time required to form a bond is significantly shorter than at lower temperatures because of increased oxygen ion mobility. The hypothesized role of oxygen ions during anodic bonding is to drift toward and react with the Si anode to form a strong interfacial chemical bond between the glass and silicon. The onset and flux of oxygen ion transport is relatively unknown. To help resolve this scientific complexity, in situ time-of-flight elastic recoil detection could be used to quantify the effect depletion layer formation has on oxygen ion migration toward the anode. Time-of-flight ERD allows for simultaneous mass and energy resolution. As a result profiles of oxygen, lithium, sodium and hydrogen ions could be performed without the risk of overlap due to energy loss in the sample, as is the case with conventional ERD. The knowledge of oxygen ion movement with respect to depletion layer formation would be beneficial to researchers in the anodic bonding field and could be used to optimize operating parameters and/or manipulate glass constituents to consistently form low temperature bonds.

As demonstrated by ERD, lithium-treated sodium borosilicate glass improves depletion layer formation at 200°C. Although direct measurement of sodium ions was not possible using conventional ERD techniques, the movement of hydrogen and alkali ions (sodium and lithium) was correlated with depletion layer formation. Furthermore, hydrogen movement towards the anode (as in the case of OH^-) was not observed suggesting that hydrogen may exist as H^+, H_3O^+ and/or H_2O in sodium borosilicate. The reference lithium concentration (Figs. 2b and 4b) is similar to the nominal sodium concentration (118 x 10^{19} ions/cm^3) in the glass. Furthermore, it is noted that a depletion of lithium ions at the near surface is compensated by hydrogen ions (Refer to the reference hydrogen profiles in Figs. 2a and 4a). Because the reference near-surface hydrogen concentration ranges between 200 and 600 x 10^{19} ions/cm^3, which is greater than the nominal alkali ion concentration (~118 x 10^{19} ions/cm^3), then if one-for-one ion exchange is assumed, the major hydrogen constituent in the glass is most likely H_3O^+.

Improved depletion layer formation at 200°C for lithium-treated as compared to untreated sodium borosilicate glass enhances bonding [25,26]. For bonding, a well defined, yet thin depletion layer is thought to be desirable to enhance the magnitude of the electric field, thus increasing the force exerted on nonbridging oxygen ions diffusing toward the anode. Most likely, at low temperatures the profile of the depletion layer is more significant than at high bonding temperatures because of decreased ionic mobility. Hence, the need for higher electric fields within the depletion layer at low bonding temperatures is critical. Because of improved depletion layer formation during electrolysis, lithium-treated sodium borosilicate may be used as an alternative bonding glass to form reliable, low temperature anodic bonds.

CONCLUSION

In situ ERD measurements show that depletion layer formation is highly dependent on temperature and alkali ion concentration. Lithium-modification of sodium borosilicate glass improves low temperature (200°C) depletion layer formation. An increase in hydrogen movement away from the anode was observed for untreated and lithium-treated sodium borosilicate at 250°C.

ACKNOWLEDGEMENTS

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