Detailed characterization of anodic bonding process between glass and thin-film coated silicon substrates


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Abstract

Anodic bonding between Si-based and glass substrates has been characterized in detail. The effects of magnitude of the applied voltage, surface properties (coating of Si substrate), and surface cleanliness (pre-bonding cleaning procedure) on the time required for complete bonding were thoroughly studied. First, the generic bonding time versus applied voltage plot was found to be concave in shape (viewed from the origin). For bonding between p-type Si substrate and Corning 7740 glass pre-cleaned with acetone, the time required was cut down from 38 to 4 min if the applied voltage was increased from 200 to 500 V. Second, the bonding time required for five Si-based substrates in ascending order was determined to be Si (p-type), polysilicon, silicon nitride, silicon oxide and then Si (n-type). Third, the bonding between p-type Si substrate, pre-cleaned with H₂SO₄–H₂O₂ and HF, and Corning 7740 glass was completed within 1 min, which was much faster than that pre-cleaned with acetone (4 min). Finally, from bonding point of view, Corning 7740 glass was superior to Corning 7059 glass and Fisher slide due to its thermal coefficient of expansion matching with the underlying Si substrate and the presence of significant amount of sodium ions in the glass. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Over the past decades, various bonding techniques have been used extensively in the integrated circuit (IC) industry for the packaging of pressure sensors and accelerometers as well as the construction of complex microchemical reactor [1]. These techniques can be categorized into direct, intermediate layer, and anodic bondings. Direct bonding places stringent requirements on the cleanliness and flatness of the surfaces to be bonded and it requires a high temperature annealing to establish high strength bonding. Intermediate layer bonding resembles direct bonding except that an additional layer is deposited to lower the annealing temperature of the bonding process. Anodic bonding is gaining significance in micro-Total Analysis Systems (μTAS) and miniaturized biological reactors because of its promising use in sealing Si and glass-based microfluidic devices under an applied voltage of 100–1000 V [1–4]. It offers advantages of high bond strength at moderate or low processing temperature (≈ 200°C–400°C).

Deterministic parameters for anodic bonding include magnitude of applied DC voltage, temperature, nature of surfaces to be bonded, and bonding time. Research groups in this field have done a lot of work investigating the effects of applied voltage and temperature on the bondability and the final strength of the bonded pieces such as the tensile strength [2,3] and interfacial fracture toughness [4]. Nevertheless, to our knowledge, little attention was paid to characterize the time required for a complete bonding at different operating conditions. There are a number of factors influencing the bond strength and the bonding time required in a typical Si-glass anodic bonding process. Among them, the cleanliness [5] and chemical nature of the to-be bonded surfaces are essential. Often, glass favourable for bonding exhibits a close thermal coefficient of expansion (TCE) to that of the underlying Si. However, from device fabrication point of view, such glass may not be easily patterned and etched, or vice versa.

In this work, anodic bonding process for thin-film coated Si substrates and glass materials is investigated in detail. First, the time needed for a complete bonding (hereafter termed as bonding performance) at different applied voltages is evaluated. Second, the bondability between thin-film coated Si substrates and Corning 7740
glass is investigated. Third, the effect of surface pre-treatment and cleanliness on the bonding performance is discussed. Finally, bonding quality and performance between p-type Si substrate and different glasses are studied.

2. Experimental

2.1. Experimental setup

The bonding system comprised of a hot plate, a DC power supply (HP6035A, USA) together with a pair of Pt electrodes, and ceramic bars. Pre-cleaned Si and glass substrates were sandwiched between the pair of Pt electrodes. Then, the ceramic bars and screws were used to fix the bonding pair including the electrodes. The same number of turns was applied to the screws to avoid the undesired load effect [4]. The assembly was heated to 300°C and a DC voltage was applied to the electrodes, ensuring a positive electrode potential on the Si side with respect to the glass.

2.2. Preparation and cleaning of pre-bonding substrates

In this study, five Si-based substrates were prepared for the bonding experiments, which were bare (p-type and n-type) and thin-film coated (polysilicon, silicon nitride, and silicon oxide) Si wafers. The bare Si used was 550 μm single-side polished and (100) oriented. Polysilicon (300 nm) and silicon nitride (100 nm) films were deposited using low pressure chemical vapour deposition (LPCVD) process, and silicon oxide (100 nm) was grown by dry thermal oxidation. Process conditions for the preparation of these surfaces are detailed in Table 1. For glass materials, three types of which were investigated including Corning 7740 glass (500 μm), Corning 7059 glass (500 μm), and Fisher slide (1000 μm). Si and glass wafers were cut into 2 cm² square-shaped pieces using a diamond cutter, with the size of glass made slightly larger than that of Si to prevent possible electrical discharge during the bonding process.

Two cleaning procedures were employed in the experiments. One utilized acetone to pre-clean glass surfaces as well as some specific Si substrates prior to the bonding. In the other one, solutions of H₂SO₄–H₂O₂ and HF were applied to clean Si-based substrates. Si was first immersed in a 10:1 H₂SO₄–H₂O₂ mixture at 120°C for 10 min. It was then dipped into a HF bath (HF:H₂O ≈ 1:100) at room temperature for 1 min. Finally, the surface was rinsed with DI water.

2.3. Determination of bond completeness

Initial attempt has been made to visualize the bonding quality using infrared (IR) detector. However, due to the size effect of the bonded piece, the resolution was not good enough to view bubbles formed between the bonded Si and glass. One simple alternative used in this work to measure the bond completeness was to calculate the area percentage occupied by bonded regions using naked eyes. For example, dies with 60% bonding and complete bonding are illustrated in (a) and (b) of Fig. 1. The unbonded areas are indicated by the interference fringes.

<table>
<thead>
<tr>
<th>Thin-film material</th>
<th>Deposition process</th>
<th>Gas flow (sccm)</th>
<th>Temperature (°C)</th>
<th>Pressure (Torr)</th>
<th>Deposition rate (nm/min)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysilicon</td>
<td>LPCVD</td>
<td>SiH₄ = 70</td>
<td>620</td>
<td>0.3</td>
<td>8</td>
<td>300</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>LPCVD</td>
<td>NH₃ = 64</td>
<td>840</td>
<td>0.2</td>
<td>4</td>
<td>100</td>
</tr>
<tr>
<td>Silicon oxide</td>
<td>Thermal oxidation</td>
<td>N₂ = 100</td>
<td>900</td>
<td>760</td>
<td>1.9</td>
<td>100</td>
</tr>
</tbody>
</table>

Fig. 1. A pictorial representation of the bonding pair between p-type Si and Corning 7740 glass, which were pre-cleaned with acetone. The bonding was carried out at an applied voltage of 500 V. (a) Picture taken at 2 min of the bonding process, showing 60% bonding. (b) Picture taken at 4 min of the bonding process, showing a complete bonding.
As there is difficulty using the current setup to visualize the bonding front in-situ, the method of bisection was then used to determine the process end-point. For instance, if a bonding duration of 30 min resulted in 100% bonding whereas that of 10 min resulted in 50% bonding, then experiment with bonding time of 20 min would be further carried out. Suppose this resulted in 100% bonding, bonding time of the next experiment would be set to 15 min. If bonding duration of 20 min did not result in 100% bonding, then bonding time of the next experiment would be set to 25 min. This procedure continued until satisfactory level of confidence for accurate determination of the required bonding time was achieved, i.e. within 10% error. The bond strength of the finished sample was determined using Instron 5567 tensile testing machine (USA).

3. Results and discussion

3.1. Effect of applied voltage

Anodic bonding between Si and Corning 7740 glass, both pre-cleaned with acetone, was investigated. Fig. 2 shows the plot of the bonding time required at different applied voltage conditions. As can be seen from the figure, the required bonding time drops significantly as the applied voltage increases from 200 to 500 V. This can be explained with respect to the bonding mechanism discussed below [1,6].

At an elevated temperature, Na\textsuperscript{+} ions in the glass become so mobile that they are attracted toward the cathode as a result of the applied voltage. This leaves behind relatively immobile oxygen anions at the glass side of the Si-glass interface, at which a space charge region is formed. This in turn creates an equivalent positive charge (image charge) on the Si side of the Si-glass interface (as illustrated in Fig. 3), resulting in a high electric field (magnitude of up to 10\textsuperscript{6} V cm\textsuperscript{-1} [7,8]) across the Si-glass interface. Under the high electric field, oxygen anions are drifted away from the Na\textsuperscript{+} depletion region to the Si surface. As this happens, oxidation of Si by the oxygen anions is presumed to occur and a thin oxide layer is formed at the interface, which contributes to the migration of the bonding front.

However, at a small applied voltage, i.e. a reduced electric field, the drift velocity and the kinetic energy possessed by the oxygen anions cannot sustain a high oxidation rate at the bonding front of the Si-glass interface, thus a longer bonding time is required. As the electric field becomes negligible, reaction extinguished at the interface and no bonding can be achieved. We have observed that, in the absence of an electric field, there was no indication of bonding even after 6 h of experiments.

The bonding current as a function of time is illustrated in Fig. 4. A drastic current drop was observed in the first minute of the bonding experiments, which is partly due to the surge of Na\textsuperscript{+} ions drifted to the cathode. As the migration of Na\textsuperscript{+} continues, the accumulation of positive charge repels the incoming ions and the current reaches a steady state at a longer time.

3.2. Effect of Si surface properties

Table 2 presents the bonding time required between the five Si-based substrates and Corning 7740. The bonding time required in ascending order is Si (p-type) < polysilicon < Si\textsubscript{3}N\textsubscript{4} < SiO\textsubscript{2}. Si\textsubscript{3}N\textsubscript{4} and SiO\textsubscript{2} are dielectric materials, which prevent the positive image charges from reaching the silicon nitride–glass interface. Instead, the image charges are accumulated at the silicon nitride–Si
Table 2
Bonding time required between the five Si-based substrates and Corning 7740 glass. Corning 7740 glass was pre-cleaned with acetone while the Si-based substrates were pre-cleaned either with H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF solutions. Bonding was also performed at two voltages.

<table>
<thead>
<tr>
<th>Wafer</th>
<th>p-type Si</th>
<th>n-type Si</th>
<th>Poly Si</th>
<th>Si\textsubscript{3}N\textsubscript{4} / Si</th>
<th>SiO\textsubscript{2} / Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonding time</td>
<td>4</td>
<td>&gt; 20</td>
<td>20</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>(min)\textsuperscript{a} at 500 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bonding time</td>
<td>1</td>
<td>5</td>
<td>30</td>
<td>15\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>(min)\textsuperscript{b} at 500 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bonding time</td>
<td>15</td>
<td>30</td>
<td>60</td>
<td>25\textsuperscript{c}</td>
<td></td>
</tr>
<tr>
<td>(min)\textsuperscript{b} at 400 V</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Pre-cleaned with acetone.
\textsuperscript{b} Pre-cleaned with H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF.
\textsuperscript{c} HF dip was excluded for this wafer.

interface. This significantly reduces the electrostatic force at the bonding interface and slows down the bonding process.

As given in Table 2, the bonding performance of p-type Si is much better than that of n-type Si. P-type Si (boron-doped) is electron deficient whereas n-type Si (phosphorous-doped) is electron rich. Under an electric field, positive image charges are readily formed at the Si side of the Si-glass interface for p-type Si and the high electrostatic force thus developed is conducive to rapid bonding. On the other hand, the formation of positive image charges is quite difficult for n-type Si, and no noticeable bonding was observed even if a voltage of 500 V was applied for more than 20 min.

3.3. Effect of surface pre-treatment

Two cleaning procedures were selected and compared, details of which are stated in Section 2.2. The bonding performance between p-type Si and Corning 7740 (pre-cleaned with acetone) was well characterized previously and is taken as a reference for comparison with the second cleaning method (H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF). The generic bonding time versus applied voltage curves for the two cleaning methods are compared in Fig. 5. It can be seen that H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF cleaning provides better bonding performance than acetone cleaning. At an applied voltage of 500 V, the bonding time required for the former was reduced to 25% of that for the latter cleaning. Acetone can only be used to wash away particulates and loosely attached organic residues, but fails to remove native oxide and the other trace contaminants on the surface, which are retarding the bonding process. In this regard, H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF helps to remove these contaminants so as to speed up the process.

H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O\textsubscript{2} and HF cleaning also shows improvement for the bonding of other Si-based substrates, as summarized in Table 2. Furthermore, as lower voltage bonding is sometimes desired for protecting device components from damage, the bonding performance of the thin-film coated Si substrates at lower voltages is also given in Table 2.

3.4. Effect of glass properties

The TCE of Fisher slide is very different from that of Si. So when they were bonded at high temperature (300°C), in spite of similar bonding time compared with that of Corning 7740, serious cracking in the slide was observed as a result of a large thermal stress developed at the interface during the cooling stage of the process [9]. One way to eliminate the cracking phenomenon is to bond Si and Fisher slide at lower temperature. At a temperature of 150°C, bonding was completed in 60 min at an applied voltage of 500 V, without any fracture in the slide surface.

Apart from TCE matching, sodium ion concentration of the glass substrate has significant effect on the bonding performance. Although Corning 7740 and Corning 7059 glass have similar TCE values (3.25 × 10\textsuperscript{-6} K\textsuperscript{-1} for the former one and 4.6 × 10\textsuperscript{-6} K\textsuperscript{-1}) and are close to that of Si, the bonding time of 7740 was at least an order of magnitude shorter than that of 7059. When bonded with p-type Si pre-cleaned with acetone at an applied voltage of 500 V, 7740 took 4 min for a complete bonding while 7059 showed no sign of bonding even for a bonding duration of 30 min. This was due to the low Na\textsubscript{2}O concentration in 7059 (\textlessthan; 0.3 wt.%) compared to 7740 (3.8 wt.%), resulting in a reduction of electric field at the bonding interface and slows down the bonding process.

3.5. Bond strength

Preliminary testing has been carried out to evaluate the tensile strength of the bonded pair. The bond strength for those that are completely bonded is greater than 15 MPa, whereas for those that have significant unbonded regions (bonding < 90%), the bond strength is below 10 MPa.
observed that the glass often breaks along the boundary of the trapped air bubble for those of incomplete bonding.

4. Conclusions

The effects of voltage, surface properties, and surface cleanliness on the bonding time required for anodic bonding between Si-based substrates and glass have been addressed. It was found that the magnitude of the applied voltage had great influence on the bonding time. For bonding between p-type Si substrate (pre-cleaned with acetone) and Corning 7740 glass, the bonding time required at an applied voltage of 500 V (4 min) was only 10% of that at 200 V (38 min). Besides, bonding with p-type Si substrate was preferred over n-type Si substrate. The bonding time required for different thin-film coated Si substrates in ascending order was Si (p-type) < polysilicon < Si₃N₄ < SiO₂. Even with an applied voltage of 500 V, the bonding of SiO₂ (pre-cleaned with acetone) took 90 min. Then, instead of acetone pre-cleaning, H₂SO₄–H₂O₂ and HF cleaning was used to provide significant reduction in the bonding time for all surfaces. With this, the bonding time required for SiO₂ dramatically reduced to 15 min. Finally, the comparisons among Corning 7740, Corning 7059 and Fisher glass manifested the importance of TCE matching as well as the role of sodium ions for a successful bonding. Further studies will be conducted to disclose the reaction occurring at the interface and to come up with better cleaning procedure for Si and glass substrates so as to achieve ultra-fast anodic bonding process.

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References