The highly useful phenomenon—that silicon (with a thin oxide layer) may form an impressively strong bond to glass when the two materials are brought into intimate contact under the influence of strong electric fields and high temperature, anodic bonding (also known as “Mallory bonding,” named after the company where it was invented and patented)—has been known and used for many years.\(^1\)

The process is particularly useful for microelectromechanical system (MEMS) pressure sensors and other transducers and in weather sealing of solar cells because the bond hermetically seals the surfaces together.\(^3\) In our research group we use the process for sealing \(\mu\)-reactors for catalyst characterization;\(^4\) however for this application the high temperatures needed for successful anodic bonding may cause catalysts to sinter or otherwise lose activity. An example of this is Au-based catalysts, which are notorious for deactivating since activity is dependant on very small Au particle size. This paper describes a practical way to overcome this issue by locally cooling the chip while the rest of it bonds. This method has proven practical and reliable in our implementation and could be useful for many other MEMS applications.

In brief, anodic bonding works by applying a large (\(\sim\)kV) negative bias on the glass with respect to the silicon while at the same time heating the stack such that cations in the glass become somewhat mobile. The electric field set up over the interface causes migration of ions (typically Na\(^+\) for normal glass types) away from the interface, which sets up an intrinsic electrostatic attraction between the silicon and the glass. No external force is therefore required as the internal forces set up by this field are very strong (pressure in the GPa range).\(^5\)\(^6\) True chemical bonds are formed between the Si and the glass permanently bonding the two surfaces. A schematic of the process is shown in Fig. 1. The downside of the technique is the inherent necessity of elevated temperatures to give the cations reasonable mobility in the glass.\(^6\)

In some applications a typical bonding procedure for borosilicate-type glass (e.g., Pyrex) to silicon (e.g., 30 min at 350°C) may well exceed the thermal budget of parts of the device. In such cases the traditional remedy is to use glass types that conduct at lower temperatures. A typical strategy might be a lithium doped glass-ceramics,\(^7\) but generally the process still does not work below perhaps 160°C,\(^7,8\) and differences in thermal expansion coefficients might be problematic for these glass types, while conventional borosilicate glass is well matched to Si. Another method is low-temperature soldering with, e.g., In/Sn eutectic mixtures;\(^9\) however necessary measures to avoid oxidation of the solder make this method unsuited for general use in open air, and the minimum temperature for this method is also \(\sim\)160°C. Devices may also be sealed with adhesives, but (un)cleanliness and leakage makes this unattractive.

Conventional (hot) anodic bonding is shown in Fig. 1, while the locally cooled-bonding method we have developed may be seen in cross section in Fig. 2. There are a few key differences to note. First, since it is the glass (not the silicon) that needs to be warm we apply heat from the glass side. The heater also serves as high tension cathode. Second, the heater only touches the glass where bonding is needed and heat is acceptable. Third, we have introduced a heat sink (cold finger), which also serves as electrical connection to ground, and the heat sink only touches the silicon in the areas where low temperature (not bonding) is needed. In our setup, the cold finger supporting the silicon and the hole in the heater are both cylindrical, giving the advantage of radial symmetry (no corners with stress concentration) when parts of the system heat and cool.

As a practical method for heating the top electrode, we use two commercial 150 W incandescent lamps with quartz envelopes (Osram) embedded in holes in the top electrode, which is made of aluminum for its high thermal conductivity. Quartz is insulating well above the relevant temperatures, so the power supply for the filaments does not need galvanic isolation and is indeed grounded in our setup. The heat sink is machined from copper and has internal channels for coolant flow. It is kept at a constant temperature (typically 6–12°C, but this could well be lower if needed) using a commercial circulating cooling bath. Thermal contact between the silicon and the Cu pillar may be assured with conventional heat sink compounds or a thin indium foil. For our conditions (1 kV potential drop and 475°C cathode temperature), bonding is normally complete within 20–25 min.
In order to find out what the temperature inside the reactor is during bonding, we have performed a direct measurement inside the reactor using resistive temperature detection (RTD) and also carried out a finite-element-type calculation using the COMSOL MULTIPHYSICS 3.5 software package. For the four-point RTD measurement, we have used our standard RTD μ-reactor lids, which incorporate a 100 nm thick platinum four terminal resistor structure and contact pads for making the four connections, as may be seen in Fig. 1 and detailed in Ref. 4. For the purpose of measuring the temperature inside the μ-reactor during bonding, we turned the lid “upside down” so that the Pt RTD was inside the μ-reactor. As a result, the measured RTD temperature corresponds to the temperature inside the reactor. The temperature of the aluminum top cathode was also recorded using a K-type thermocouple. The measurements are plotted in Fig. 3. It is seen that the cathode stabilizes at \(-475°C\), while the RTD temperature inside the reactor only reaches 45°C.

In the finite element analysis (FEA), the real bonding arrangement was approximated with an axially symmetric geometry similar to the actual setup. The steady state temperature distribution was computed. The geometry of the FEA and the predicted temperature distribution are shown in Fig. 4. In the bonding setup a thermal contact resistance is expected between the aluminum and Pyrex. This was represented in the simulations by a narrow subdomain along the aluminum-Pyrex interface, giving rise to a thermal contact resistance of \(5 \times 10^{-5} \text{ m}^2 \text{ K W}^{-1}\). In the FEA a constant tem-
temperature of 475°C was applied to the right boundary of the aluminum block. The bottom of the copper block was set to a constant temperature of 12.5°C, and the reaction chamber was treated as containing atmospheric air. The FEA gives detailed information about the thermal gradients from which, e.g., heat fluxes and thermal expansion can be extracted. Figure 5 shows the temperature in the reaction chamber as a function of radial position according to the FEA. It is seen that the predicted temperature is below 90°C everywhere and below 50°C within the central 8 mm diameter circle in the chamber. In the center of the chamber the FEA predicts a temperature of around 40°C, which is in good agreement with the experimental result 45°C (Fig. 3).

For evaluation of the scalability of the method, it is useful to consider a design where the radial distance between heater and cold finger edges is sufficient to ensure that a region (outside the cooled air-gap region) of purely radial heat flow exists. In the present system such a region would be the cylindrical cross section with a radius of ~5.2 mm (to good approximation). In that region the ratio of heat flows in glass $P_{G,i}$ and silicon $P_{Si,i}$ is $P_{G,i}/P_{Si,i} = (\kappa_{G}h_{G})/(\kappa_{Si}h_{Si})$, while the total heat flow is $P_{tot} = P_{G,i} + P_{Si,i}$, and where $\kappa$ and $h$ are the thermal conductivities and material thicknesses, respectively. Then, by continuity, in the reactor region the heat flow in the glass will be directed through the air film in the reactor and cause a (mean) temperature difference $\Delta T = P_{G,i}h_{air}/(\kappa_{air}\pi a^2)$ between top and bottom of the reactor; $a$ is the radius of the reactor chamber. It follows that $\Delta T$ will increase approximately linearly with reactor height; in the present design $\Delta T \approx 4$ K at $h_{air} = 3$ μm, and if arbitrarily the upper acceptable limit is $\Delta T_{max} = 60$ K, then the upper limit on the reactor chamber height is $h_{air} \leq 45$ μm, with all other parameters unchanged. Thus, the limit on reactor chamber height may be lifted if forced convection cooling is applied to the glass lid surface through the center bore of the heater.

An increase in the thickness of the glass wafer is also seen to cause an increase in $\Delta T$, but at the same time the heater temperature must be increased since $P_{Si}$ must be maintained to keep the temperature $T_{H}$ at the bonding interface fixed.

In the heater and cold finger regions, the heat flow is three-dimensional. The transition to a radial heat flow in the heater region takes place on a length scale that is approximately $h_{S} + h_{Si}$, while at the cold finger the transition takes place on a length scale of approximately $h_{Si}$ since here, the main heat flow is in silicon. It follows that the radial distance between heater and cold finger edges must fulfill $\Delta r_{min} \geq h_{S} + 2h_{Si}$. Moreover, in the region directly above the cold finger, the length scale of the temperature variation is $h_{Si}$, and thus the cold finger radius must fulfill $r_{Cu} > h_{Si}$, say, $2h_{Si}$. A minimum applicable chip size could then be estimated from $r_{min} \approx 2(h_{Si} + h_{G} + 2h_{Si} + w_{H})$, where $w_{H}$ is the width of the glass-heater contact; this probably has to fulfill $w_{H} > h_{G} + h_{Si}$, making $2r_{min} \approx 2(5h_{Si} + 2h_{C}) = 5.5$ mm with a cold finger radius $r_{Cu} = 0.7$ mm. This design was verified by FEA.

With the current design, the temperature $T_{Re}$ in the center of the reactor (on the silicon side) is almost entirely controlled by the Cu cold finger $T_{Re} = T_{L} + R_{Cu} P_{tot}$, where $T_{L}$ is the cold finger temperature (we have used $T_{L} = 12^\circ$C) and $R_{Cu} = L_{Cu}/(\kappa_{Cu} \pi r_{Cu}^2) + 1/(4\kappa_{Cu} r_{Cu} C_{Cu})$ is the thermal resistance of the cold finger of length $L_{Cu}$ including thermal spreading resistance to the Cu bulk. It follows that the reactor temperature is linearly dependent on the cold finger temperature, linearly dependent on the total heat flow, and strongly dependent on the cold finger geometry. This also emphasizes the importance of ensuring good thermal contact between silicon and the cold finger; thus we use thermogrease at that junction.

By heating from the glass side of the glass-silicon stack and providing efficient local cooling, we have shown that silicon may be anodically bonded to glass successfully while keeping small (< 1 cm) areas at ambient temperatures. This is highly useful for any MEMS or lab-on-a-chip devices, which contain heat-sensitive components such as polymeric structures or coatings, antibodies, or other biomolecules or sensitive metallic structures. The method may be scaled down to bond individual chips as small as ~5.5 mm in diameter while keeping 1.4 mm diameter regions cold. Even smaller dimensions are possible with thinner silicon and Pyrex. Cavities up to ~45 μm deep may be used in the existing setup, while still keeping the reactor temperature below 100°C. Finally, it should be possible to locally cool multiple areas/chips simultaneously when bonding whole wafers.

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