Lithium aluminosilicate glass-ceramics for low-temperature anodic sealing of MEMS sensors

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Abstract. The results of a study of the anodic bonding parameters of transparent glass-ceramics based on lithium aluminosilicates which are promising as structural materials of MEMS and MOEMS sensors are presented. A comparison of the optical transmittance of these materials and classical for MEMS industry glasses has been carried out. The glass-ceramics electrical conductivity in a wide temperature range has been measured. The procedure of hermetic sealing of glass-ceramics by the anodic bonding at temperatures of 150 – 250 °C has been worked out. A prototype of glass-ceramic atomic cell has been fabricated.

1. Introduction

For the correct operation of various microelectromechanical (MEMS) sensors, an inert atmosphere or vacuum on the chip level is often required, as well as the optical transparency of the substrate. Such devices include lab-on-chip, quantum magnetometers and atomic clocks, gyroscopes, accelerometers and pressure sensors with optical measurement scheme, bolometers and other MEMS. For hermetic sealing of such devices on a wafer level, various bonding technologies are used, the most widespread of which is the high-temperature anodic bonding of silicon and glass wafers [1]. Materials for the anodic bonding are special borosilicate glasses (in the case of silicon technologies, it is Borofloat 33, Pyrex 7740, Hoya SD-2, etc.). These glasses have high ionic conductivity at anodic bonding temperatures (about 300 – 500 °C), optical transparency, thermomechanical compatibility with other sensor materials [2]. At the same time, high voltages and temperatures required for high-quality anodic bonding of commercial borosilicate glasses, fixed coefficient of thermal expansion (CTE) and a number of other factors limit the application of this technology for some types of MEMS.

Transparent glass-ceramics can become alternative materials for anodic sealing of MEMS because of many advantages over glasses – high working temperature, low gas permeability, low fragility, high strength, thermal shock resistance, durability during mechanical processing [3]. Glass-ceramics based on lithium aluminosilicates (LAS) are promising structural materials for MEMS sealing since the CTE of LAS glass-ceramic can be adjusted within a wide range by changing composition and heat-treatment schedule. Depending on the ratio of the crystallization phases in Li\textsubscript{2}O-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} systems, some of which have a negative CTE (eucryptite), others have a positive CTE (spodumene, quartz-like solid solutions), a glass-ceramic material with a negative, zero or positive CTE is formed. Therefore CTE of LAS glass-ceramics may be approximately matched to that of silicon [4]. Successful attempts have been made to synthesize the LAS glass-ceramic composition for anodic bonding with silicon [5] and with fused quartz (using a sputtered conductive layer) [6]. But such materials were not widespread.
in the MEMS industry because of the presence of lithium is both a positive and a negative property. Lithium ions in the glass and glass-ceramics have an increased ionic mobility compared to sodium and potassium ions. For this reason, LAS materials can be bonded to silicon at lower temperatures than conventional borosilicate glasses. But lithium also has a high rate of penetration into the gate dielectrics of field-effect transistors and into silicon itself, which prohibits the use of such materials in silicon technologies. However there are many MEMS applications where this is not an obstacle – for example, microfluidic chips for bio-diagnostics and gas cells for miniature quantum devices such as magnetometers and atomic clocks [7–9]. For chip-scale atomic clock application, the low gas permeability of the glass-ceramics will allow for an increase in the long-term frequency stability by several orders of magnitude due to a decrease in the helium and neon leak rate [10]. Anodic sealing at temperatures below 170 °C will open the way to the mass production of MEMS quantum frequency standards with organic anti-relaxation wall coatings to reduce the spin relaxation in the alkali vapor cells and increase short-term frequency stability of the atomic clock [11].

This article presents the results of the work carried out to assess the prospects for use of optically transparent glass-ceramics based on lithium aluminosilicates (LAS) for anodic sealing of MEMS.

2. Experimental details
The objects of study were polished wafers with a thickness of 0.5 to 1 mm, made of glass-ceramics synthesized on the basis of lithium aluminosilicates with compositions of 55–65% SiO2, 15–25% Al2O3, 5–15% Li2O, 5–10% TiO2, 2–4% CaO. Concentrations of the crystal phase (spodumene and β-eucryptite) varied by the duration and temperature of annealing. TiO2 was used as compound nucleation agent. The basic glasses were prepared by melting and casting. The reagents of high pure oxides were mixed, and then they were melted in quartz ceramic crucibles with mixing by quartz stirrers at 1550 – 1620 °C for 8 hours in a laboratory furnace with molybdenum disilicide heaters. The melts were cast into the pre-heated metal mold. Subsequently, the glasses were annealed at 650 – 680 °C for 30 minutes and then passively cooled to room temperature. Secondary heat treatment was carried out in a two-stage mode in the temperature range of 680 – 1000 °C.

Temperature dependences of the LAS samples CTE were measured by dilatometer Linseis L75VS1000 (monocrystalline silicon was used as reference sample). Optical transmittance was measured by spectrophotometer Shimadzu uv-3600.

The measurement of the glass and glass-ceramic electrical conductivity was carried out on laboratory equipment designed for anodic bonding of silicon and glass (figure 1a). The wafers were preliminarily divided into square samples with an area of 1 cm², and blocking electrodes made of a 500 nm thick aluminum film were deposited on both sample sides by DC-magnetron sputtering. The magnitude of the initial current peak at the moment of switching on the voltage was used to estimate the specific electrical conductivity of glass-ceramics at a given temperature. Bonding of LAS samples to each other was carried out according to the scheme shown in figure 2b. Previously, a thin polysilicon layer was deposited on the sample, which serves as an anode.

![Figure 1](image1.png)

**Figure 1.** Schemes for Si–to–LAS bonding (a) and LAS–to–LAS bonding using thin Si interlayer (b).
3. Results and discussion

For the anodic bonding development, two types of LAS glass-ceramic material were tested. First type is SO-33M glass-ceramic (Russian name is “CO-33M”), which has an average CTE close to zero and is a domestic analog of the Schott Zerodur glass-ceramic. Second type is experimental LAS samples with a CTE close to CTE of silicon. The work on the exact alignment of glass-ceramics and silicon CTE is not yet finished. To date, the best of the already synthesized samples have a slightly larger CTE (∼4·10⁻⁶ 1/K) compared to silicon (3.3·10⁻⁶ 1/K). Figure 2 shows the difference between the CTE of silicon and the CTE of one of these samples (“LAS24”) in the temperature range from 20 to 400 °C.

The measured values of LAS glass-ceramic conductivity were 2 to 3 orders of magnitude higher than that of Borofloat 33 glass in the temperature range of 150 – 250 °C, as shown in figure 3. This case made it possible to successfully carry out a hermetic anodic bonding of some glass-ceramics samples with monocrystalline silicon already at a temperature of 150 °C.

![Figure 2. Difference of CTE of sample LAS24 and CTE of silicon vs. temperature.](image)

![Figure 3. Conductivity of Borofloat 33, SO-33M and sample LAS24 vs. temperature.](image)

The obtained time dependences of the current density during anodic bonding of SO-33M and LAS24 to silicon at different voltages and temperatures are shown in figure 4. The increase in the current in the first minutes of bonding was due to the spreading of the joint spot over the entire area of the silicon sample under the influence of electrostatic force. After that, all current responses showed a purely ionic character of conductivity with exponential decrease in current over time, which indicates the formation of a depleted layer at the glass-ceramic–silicon interface (as shown in figure 1a). The area under the presented curves is equal to the passed charge spent on the depleted layer formation and is a comparative criterion for the bonding strength (minimal charge density sufficient to create a bond between the Si and the glass is 3 mC/cm²) [6].

All glass-ceramic samples provided uniform high-quality bonding to the entire silicon area at temperatures above 180 °C even when using a point cathode and low voltage (< 500 volts). The passed charge density during 30 minutes under these conditions was approximately 50 – 100 mC/cm². Bonding at a lower temperature was accompanied by a negligible charge density, even at elevated voltages (> 1000 V). This fact required the use of a distributed planar cathode. The use of an aluminum thin film electrode sputtered on the cathode side of the glass-ceramic samples made it possible to provide charge densities at the level of 10 – 20 mC/cm² when bonding was carried out at 100 – 150 °C. Samples of LAS24 glass-ceramics bonded with silicon at low temperatures and a voltage of 500 volts are shown in figure 5. The minimal temperature of a successful bonding was 110 °C. In this case, a stable sealing is achieved only under the surface of the planar electrode which is clearly visible on the left side of figure 5.
Figure 4. Current during the anodic bonding of silicon to SO-33M and LAS24 ($S = 1 \text{ cm}^2$).

Figure 5. Results of silicon-LAS24 bonding at 200 $^\circ\text{C}$, 150 $^\circ\text{C}$, 110 $^\circ\text{C}$ (from left to right).

Samples of SO-33M glass-ceramic were bonded to each other. To perform this process a thin polysilicon films with a thickness of 50 – 200 nm was deposited on the top surface of one of samples (bottom wafer). The method of DC-magnetron sputtering from a single-crystal silicon target with a resistivity of 0.1-0.12 $\Omega\cdot\text{cm}$ was used. The resistivity of the deposited polycrystalline films was 5000 times higher and was approximately 600 $\Omega\cdot\text{cm}$. This corresponded to the surface resistance of 30 $\text{MOhm}/\square$ and 120 $\text{MOhm}/\square$ for films with a thickness of 200 nm and 50 nm, respectively.

The bonding results depended on the polysilicon film thickness and the bonding scheme used, and are explained using figure 6, which shows samples bonded under different conditions at 250 $^\circ\text{C}$ and 800 V (figure 6a) and the corresponding time dependences of the bonding current (figure 6b). When the standard bonding scheme shown in figure 1a was used, the bottom LAS wafer acted as a silicon wafer, but its conductivity was provided by the lithium ion flow from the side connected to metal anode to the sputtered polysilicon film. Due to the presence of pinholes in the film, some of the lithium ions from the bottom wafer could pass through the barrier polysilicon layer and cause a local electrical breakdown of the depleted layer formed in the top wafer. Applying additional wire anode contact directly to the polysilicon film at the wafer edge did not help to completely neutralize this negative circumstance, especially for very thin films due to the their high resistance comparable to the resistance of bulk LAS glass-ceramics at bonding temperatures. As a result, the depleted layer could not be formed and the bonding interface at the edge of the wafer opposite to the point anode contained unbonded voids (central sample in figure 6a). The successful results on the SO-33M bonding were obtained when the scheme with additional dielectric plate shown in the figure 1b was used. The sample with 200 nm thick interlayer bonded in this way is shown at the left sides of figure 6a.

Figure 6. Results of SO-33M–to–SO-33M bonding using polysilicon interlayer with thickness of 200 nm (left and centre) and 50 nm (right) (a) and the time dependences of the bonding current (b).
This configuration of bonding equipment was used to fabricate a prototype of two-chamber gas cell for a chip-scale atomic clock, shown in figure 7. The cell was formed by sandwiching a glass-ceramic wafer with two through-hole cavities and connection channels between two another wafers by anodic bonding using polysilicon interlayers. Cell fabrication process is shown in figure 8.

First wafer micromachining was carried out by drilling with tubular drill bits with diamond grains binded by electroplating. The drill bits diameter was 2 and 3 mm. The wafer was fixed to the movable substrate holder by molten paraffin. The cavities formation was carried out by through-wafer sinking the drill bit at spin rate of 1000 rpm. Formation of two arc-shaped channels with a width of 200 µm was carried out by sinking the tubular drill bit to the depth of 150 µm at the center point between the cavities. After removing the paraffin in toluene, the wafer was cleaned in isopropanol, water and piranha solution. Then 200 nm thick polysilicon films were sputtered on both sides of the wafer.

First anodic bonding at 250 °C and 500 V was carried out to join the micromachined wafer to the bottom glass-ceramic wafer. The operation of the filling the cell with an alkali dispenser was not performed at the prototype manufacturing stage. Second anodic bonding at the same conditions was carried out in vacuum chamber to seal the cell by top glass-ceramic wafer. Exponential drop of the current passed through the interface during the first and second anodic bonding are shown in figure 9. The value of the second bonding current was slightly less due to the lower real temperature near the connected surfaces, as the SO-33M glass-ceramic has a low thermal conductivity. The sandwich of three SO-33M glass-ceramic samples bonded in the described process is shown in figure 10.
The transmittance spectra of Borofloat 33 glass used in the production of chip-scale atomic clock and SO-33M glass-ceramic in the range of 300 – 2500 nm were compared. As shown in figure 11, the SO-33M glass-ceramic transmits light only 2% worse than Borofloat 33 in the entire measured range. However, a near-zero coefficient of thermal expansion of SO-33M glass-ceramic is an advantage for MOEMS application.

The same bonding conditions were applied to seal SO-33M with fused quartz due to the proximity of their CTE. The bonded sandwich of SO-33M glass-ceramic and fused quartz after etching of the polysilicon layer in the optical cavity is shown in the figure 12. This technology may be promising for manufacturing of microfluidic sensors for UV diagnostics of various biomaterials and atomic cells with Hg vapours.

Figure 11. Transmittance of Borofloat 33 glass and SO-33M glass-ceramic.

Figure 12. Result of quartz–to–SO-33M bonding using polysilicon layer with thickness of 200 nm.

4. Conclusion

The hermetic anodic sealing of lithium aluminosilicate glass-ceramic wafers to each other as well as to silicon and fused quartz wafers at temperatures of 150 – 250 °C has been worked out. A prototype of glass-ceramic gas cell for chip-scale atomic clock has been fabricated. The obtained results can be applied in the technology of MEMS atomic cells and microfluidic devices.

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