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Sealing of silicon-glass microcavities with polymer filling

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Abstract. Investigation of hermetic sealing of selected polymers in silicon-glass microcavities has been presented. The anodic bonding method has been adapted for hermetic encapsulation of the polymer in microcavity. According to standard conditions of the anodic bonding process (temperature: 400°C, voltage: 1000 V), the main challenge was the significant reduction of temperature in order to avoid degradation of the polymer. An analysis of the influence of reduced temperature and oxygen-free atmosphere on bond quality has been done. Proper parameters of the anodic bonding process enabling good and hermetic encapsulation of the polymer in the microcavity as well as optimal polymer treatment have been elaborated. Studies have shown that the closure of high density polyethylene in microcavity by anodic bonding process at a temperature reduced to 340°C is possible. This procedure will be used for the fabrication of main elements for a new family of high radiation MEMS sensors.

Key words: anodic bonding, polymer filling, sealing of silicon and glass.

1. Introduction

Silicon and glass are often used as constructional and packaging materials for microsystems and MEMS sensors. These materials are the most commonly used when high resistance for aggressive chemicals [1–4] and high stability of inner atmosphere (including vacuum) [5–8] are required. Moreover, silicon-glass sensors can work where ionizing radiation occurs, e.g. in oncology [9] (low level of radiation), in space [10] (medium level of radiation), and in nuclear facilities [11] (high level of radiation).

Sealing of materials is a crucial process in MEMS technology. In the applications referenced above, permanent and ultra-stable sealing is required. Among many sealing methods used in microsystems technology [12, 13], the direct silicon-to-glass anodic bonding is highly resistant to ionizing radiation [14]. The anodically bonded structures are characterized by high bond strength [15], high chemical resistance [4] and gas tightness [16–18]. For these reasons, this method was used for the fabrication of main elements for a new family of high radiation MEMS sensors [19].

In this paper, direct silicon-to-glass anodic bonding has been used for encapsulation of small polymers portion (3 mg) inside silicon-glass microcavities (10 mm^3). The challenge was to hermetically close a polymer in protective atmosphere in order to maintain appropriate conditions for the polymer. A polymer from a group of indicators of radiation [20], which under the influence of radiation releases an amount of hydrogen proportional to the dose of radiation, has been chosen for encapsulation in microcavity.

In order to avoid degradation of the polymer, a significant reduction of temperature of the standard anodic bonding process was required. The non-standard anodic bonding process in presence of polymer, reduced temperature and oxygen-free atmosphere is necessary and is the main subject of this article. The technology developed and described here opens the way to fabricate MEMS sensors of high level of radiation. The development of high radiation MEMS sensor, including sensor technology and radiation tests, is presented in [21].

2. Technical analysis

2.1. Anodic bonding process. The direct silicon-to-glass anodic bonding is a direct sealing process in which a stable chemical bond between bonded materials is obtained. The anodic bonding process is a complicated chemical reaction, which has been shown in three main steps (Fig. 1) [22]:

- generation of electrostatic force by applied voltage – initiation of joining substrates,
- formation of depleted layer in glass by sodium ion current,
- formation of Si-O chemical bond.

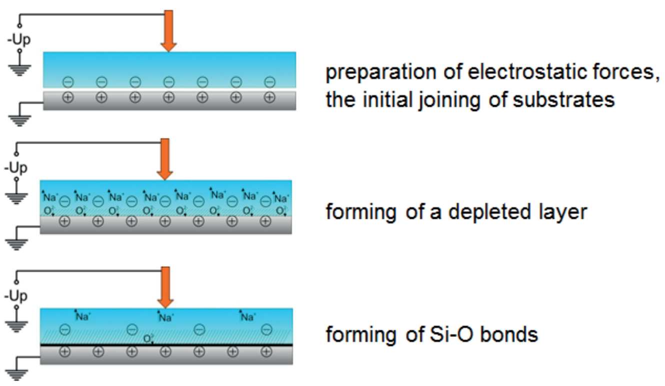

Fig. 1. Scheme of the chemical reaction steps in anodic bonding process of silicon and glass

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A stable connection of silicon and glass is obtained for standard parameters of anodic bonding process: temperature T = 400°C, voltage U = 1000 VDC, pressure p = 100 kPa, atmosphere – air [23]. A reduction of temperature of the process (Fig. 2a) as well as a voltage polarization (Fig. 2b) result in decreasing current density. It causes the slower flow of ions in the structures and smaller electrostatic forces. That entails substantial efficiency decreasing of Si-O bonds forming. In consequence, the bond quality – bond strength, chemical stability, and tightness – is reduced.

The atmosphere also significantly affects the anodic bonding process (Fig. 2c). The best results are obtained for air atmosphere.

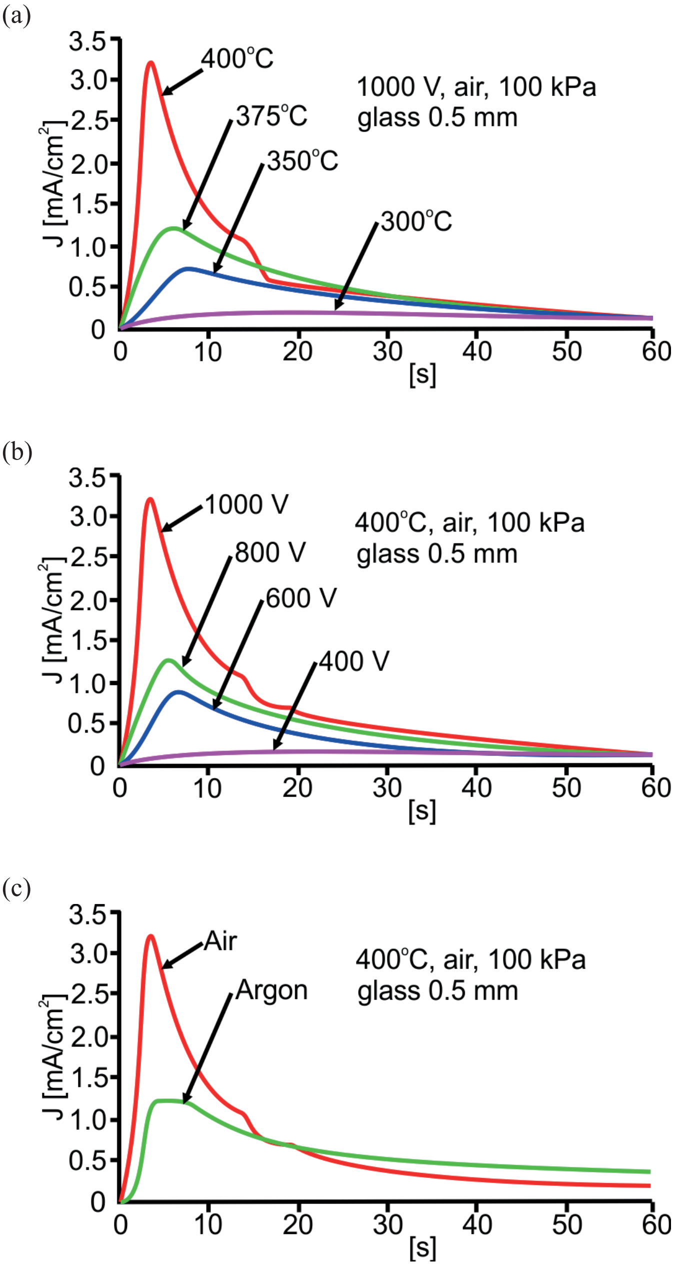

Fig. 2. Current characteristics of anodic bonding of silicon-glass Pyrex: (a) the effect of temperature; (b) the effect of bias voltage; (c) the impact of gas atmosphere [23]

2.2. Polymer for encapsulation. The parameters of the silicon-to-glass anodic bonding should be adjusted to allow for encapsulation of the polymer. The most popular polymers used as radiation indicators for high doses of radiation have been shown in Table 1 [24]. As mentioned earlier, optimum temperature for direct silicon-to-glass anodic bonding is 400°C for standard parameters. The lowest reduction of process temperature is indicated. The degradation temperature of presented polymers ranges from 180°C to 340°C. Moreover, that kind of polymers is oxidized at high temperatures (below the degradation temperature) in contact with air.

Table 1
Plastics used as indicators of high doses of radiation

Polymer	Melting temperature [°C]	Degradation temperature [°C]
Polyethylene (PE)	150	300
High Density Polyethylene (HDPE)	165	340
Polypropylene (PP)	165	300
Polystyrene (PS)	100	300
Polyvinyl chloride (PVC)	80	180
Polymethyl methacrylate (PMMA)	115	300

The high density polyethylene (HDPE) has the highest degradation temperature 340°C, is cheap and available as granules, therefore, it was selected for tests. To avoid the oxidation of the polymer in high temperature, the anaerobic nitrogen atmosphere has been used.

3. Experiment

Proper parameters of the anodic bonding process for good and hermetic encapsulation of the polymer in the microcavity have been investigated. As mentioned before, the process must be conducted in nitrogen protective atmosphere, and the maximum temperature of the process should be 340°C. The test structures with dimensions 9 × 16 × 1.5 mm^3 were manufactured. Each of the structures consisted of two layers: a monocrystalline double-side polished (100) n-type wet deeply etched silicon wafer 0.4 mm thick (ITME, Poland) and an anodically bonded glass cover 1.1 mm thick (Borofloat 33, Schott, Germany) (Fig. 3).

The micromachining procedure included KOH selective etching (80°C, 10M KOH, oxide mask) of silicon wafer. The two-step process formed the container for polymer. Following, the 3 mg of HDPE was manually placed inside the container. Finally, the sealing process for temperature in range 300–380°C and voltage in range 1000–2000 V was tested.

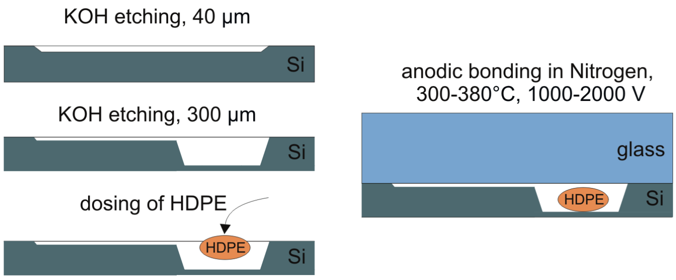

Fig. 3. Fabrication process in short

The gases were released from the polymer in high temperature (> 300°C), contaminating silicon and glass surfaces designed to be bonded. This resulted in the blocking of the anodic bonding process (Fig. 4). The anodic bonding process is sensitive to contaminations of surfaces designed to be bonded (passivation of surfaces). The reason behind the gases being released from the polymer can be absorption of gases from surrounding atmosphere (mostly steam water from several up to tens of percent) by the polymer during storage.

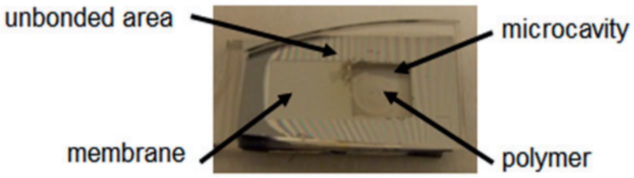

Fig. 4. Large unbonded area on the sample after dosing the polymer and anodic bonding procedure

In order to reduce water content in a polymer, as well as other absorbed gases, annealing of polymer in the vacuum before final sealing process has been done (Fig. 5). The temperature of 180°C and vacuum level of 0.3 Pa have been applied. The absorbed water and other gases have been evaporated (the polymer colour changed from white to milky).

Next, attempts to bond the test structures in different temperatures with the outgassed polymer have been taken. Anodic bonding method was ineffective at temperature below 300°C (Fig. 6a). A half-area, yet stable connection between the glass and the silicon with no apparent degradation of the polymer was obtained at temperature 320°C (Fig. 6b). The best results were obtained for a temperature of approximately 340°C and a voltage of 1500 V (Fig. 6c). No degradation of the polymer for temperature 340°C of the process has been observed. Applied voltage could not exceed 1500 V to avoid avalanche breakdown.

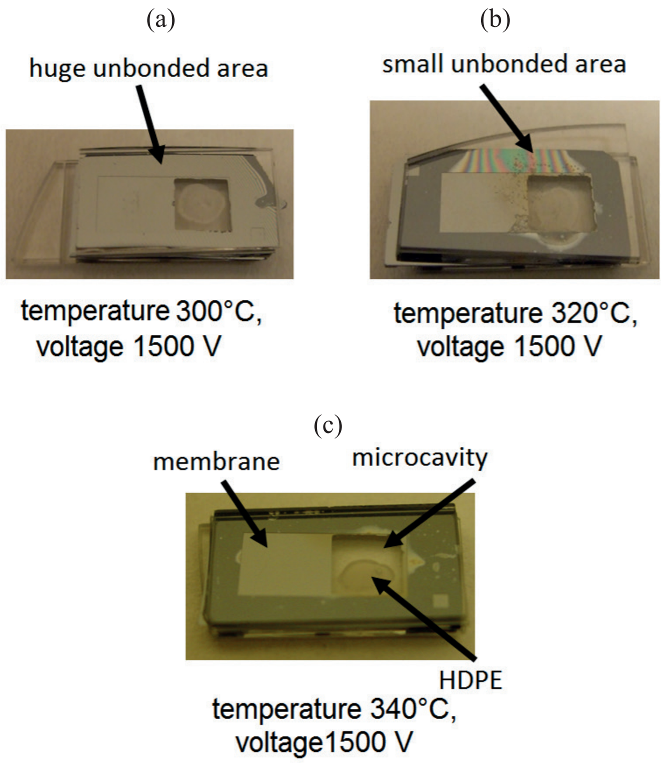

Fig. 6. The sealing polymer in the form of micropellets in silicon-glass micro-inches for the parameters of the process: (a) 300°C, 1500 V – no connection; (b) 320°C, 1500 V – partial connection; (c) 340°C and 1500 V – good connection

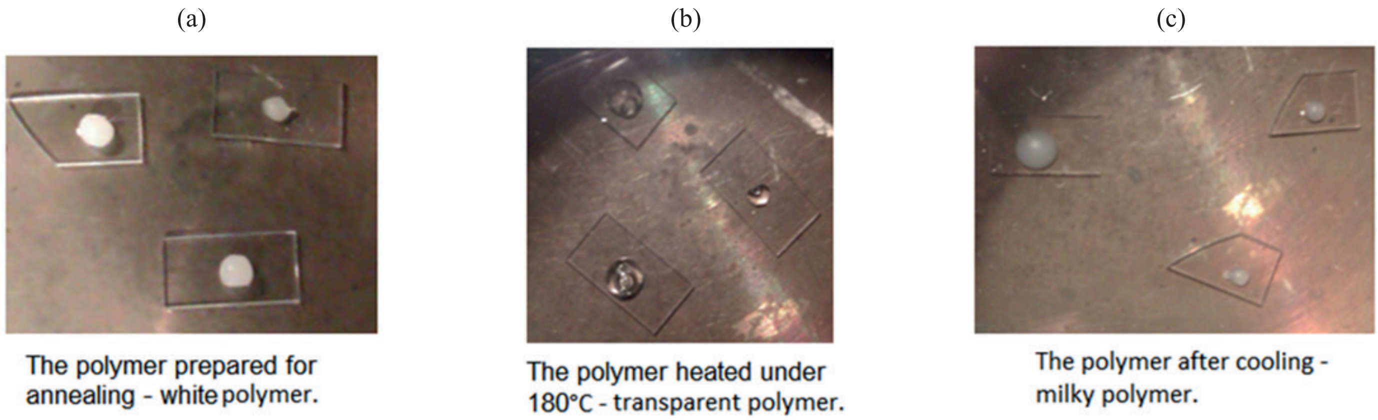

Fig. 5. The three steps of annealing the polymer in vacuum: (a) polymer prepared for annealing; (b) polymer heated under 180°C; (c) polymer after cooling

4. Conclusion

The non-standard anodic bonding process for encapsulation of polymer in microcavity has been investigated. A significant reduction of temperature according to the standard anodic bonding process in order to avoid degradation of the polymer has been done.

72 test structures for encapsulation of the polymer in microcavity by anodic bonding process have been prepared. The sealing processes for temperature in range 300–380°C and voltage in range 1000–2000 V have been tested.

The high density polyethylene (HDPE) with degradation temperature in air 340°C was selected for tests. To avoid the oxidation of the polymer in high temperature, the nitrogen anaerobic atmosphere has been used. Preliminary results have shown that polymer annealing in vacuum in temperature 180°C is required before final sealing process. This reduces the polymer outgassing at high temperature (> 300°C), which caused contamination of silicon and glass surfaces designed to be bonded.

Research has shown that the closure of polyethylene in microcavities by anodic bonding process at a temperature reduced to 340°C is possible. The use of anaerobic atmosphere allowed for encapsulation in 340°C without triggering the degradation process in the polymer.

The study on developing the procedures of direct silicon-to-glass anodic bonding at lower temperature of 340°C opens up new possibilities for encapsulation of some polymers in MEMS structures. However, the reduction of process temperature as well as reduction of voltage polarization caused the decreasing of current density. In consequence, bond quality (bond strength, chemical stability and tightness) has been reduced in theory. Another study of the bond quality seems to be necessary to fully characterize the process described here.

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