LK-5 glass surface modification by glass blowing method based on microsystem technology

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Abstract. This paper considers the possibility of modifying the surface LK-5 glass by glass blowing methods to solve the problems of creating an atomic clock and ensuring a controlled distribution of metal nanoparticles on its surface. The evolution of the formation of a spherical profile of a glass surface on a hermetically welded cavity in a glass-silicon system was studied experimentally and theoretically. Also, the possibility of modifying the spatial parameters of arrays of nanoparticles distributed on the glass surface has been demonstrated. The obtained experimental and theoretical data demonstrate sufficient convergence.

1. Introduction

The applying of glass substrates as a structural material has become widespread in various sensor applications used in biomedicine, optics, photonics, plasmonics, and microelectromechanical systems (MEMS) [1]. Various technological methods have been developed for the integral fabrication of microfluidic channels, photonic waveguides, and microlenses, such as laser ablation [2], abrasive-jet blasting [3], reactive ion etching (RIE) [4], and femtosecond laser irradiation and chemical etching (FLICE) [5]. Recent studies in the field of creating integral cells of atomic clocks have shown the possibility of using glass blowing methods to produce spherical cells at the wafer level [6]. This technology is based on the formation of glass spheres under the influence of excessive pressure at glass softening temperatures. Excess pressure is formed when the gas is heated in a hermetically sealed cavity. It is a cylindrical hole etched in silicon using deep plasma-chemical etching, sealed with a glass substrate (Pyrex) using an anodic bonding. This paper considers the possibility of modifying the surface LK-5 glass by glass blowing methods to solve the problems of the produced atomic clock and ensuring a controlled distribution of metal nanoparticles on its surface.

The change in the profile of the glass surface is accompanied by a thinning of its thickness and an increase in the surface area. This can be used to modify the distribution of arrays of metal nanoparticles deposited on the glass surface. At the same time, the technology of creating these arrays, which consists in high-temperature annealing of thin metal films deposited on such surfaces as SiO₂, TiO₂, NiO, etc. [7], is compatible with the technology described above. Such arrays of Au, Ag, Al nanoparticles have become widespread due to the surface plasmon resonance effect. Parameters as the particle size, shape, and density of their arrangement largely determine the parameters of the plasmon resonance: wavelength, intensity of photon absorption and reflection of photons. Increasing the area of the upper glass surface should lead to stretching of the array of nanoparticles, which can be used as a method for modifying the array parameters.
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2. Experimental results

2.1. Fabrication

The structures of the sealed cavities were fabricated on standard silicon substrates 350 µm thick and LK-5 glass 485 µm thick. The technological route is shown in Figure 1. Cylindrical cavities in a silicon substrate were formed by deep plasma-chemical etching in the BOSH mode (Figure 1b). The etching depth was 200 µm with a variation in the cavity diameters in the range of 500-1500 µm. In contrast to the works given in [6], where non-standard thick silicon substrates (more than 1 mm) were used, the creation of cavities with a greater depth is impossible due to the limitations of the stiffness of the formed silicon membrane at the bottom of the cavity, so that its thickness would be about 150 µm. The anode bonding of the wafer was carried out at a temperature of 400 °C in the air (Figure 1c). To study the formation of a spherical glass surface, the wafer was divided into 1x1 cm chips by a circular saw. The study was carried out during high-temperature annealing in a muffle oven in the temperature range of 850-950 °C and the time range from 5 to 60 minutes (Figure 1d). The samples cooled at the end of annealing at room temperature. The tendency of deformation of glass with a thickness of 200 µm was also investigated. The glass was thinned by wet etching methods. The profile of the formed structures was studied using the AmbiosXP-1 profilometer.

To investigate the possibility of ensuring a controlled distribution of metal nanoparticles, an Au film 2 nm thick was deposited on the glass surface before annealing. The gold film was applied using a vacuum thermal evaporation unit. After applying the gold film, the samples were also annealed at a temperature of 950 °C with a duration of 15 minutes. The distribution of nanoparticles was monitored using SEM.

2.2. FEA of viscoelastic deformation of glass.

The glass blowing process was also analyzed using numerical simulation methods. Heating LK-5 glass to temperatures above 820 °C leads to glass softening and a significant decrease in its viscosity to values below $10^7$ Pa·s [8]. This means that the deformation of the glass under the influence of pressure can no longer be determined only by elastic deformation and must be described using viscoelastic
models. To describe this behavior, the Oldroyd-B model was used, which includes the viscosity and relaxation time. It should be noted that in this formulation, the internal stresses of the glass after the anode bonding of the wafer, caused by the difference in the temperature coefficients of expansion of the glass and silicon, were not taken into account.

The numerical modeling was carried out in a two-dimensional axisymmetric formulation, which can significantly reduce the cost of computing resources. The geometry of the calculated model includes a cross-section of the glass above the cavity, which can deform under the influence of pressure in the cavity, and a fixed cross-section in the zone of connection with silicon. The fixing corresponding to the welding zone was set along the lower border of the glass. The upper boundary of the glass is defined by a free surface with the possibility of deformation and atmospheric pressure acting on it. The pressure in the cavity was determined based on the equation of state for an ideal gas with allowance for glass deformation. The initial value is determined by the increase in pressure in the sealed cavity due to a temperature change. It is assumed that at the time of the anode bonding, the pressure in the cavity is equal to atmospheric pressure. Under the influence of overpressure occurs glass viscoelastic deformation and volume change of the cavity. The resulting pressure on the lower boundary of the glass above the cavity is determined as the difference between the external pressure and the initial pressure in the cavity during heating, and further due to the deformation of the glass, the volume of the cavity increases and the pressure decreases.

Numerical simulations were carried out in the time domain in the range from 0 to 60 minutes. The load is set as a smooth function of time to reduce non-linearity at the initial stages of the process.

3. Results

After high-temperature annealing, deformation of the upper glass surface in the region above the cavity was observed on the samples (Figure 2a). During prolonged annealing (time more than 30 minutes), the edges of the glass were shattered and a rim was formed along the perimeter of the chip, which made it impossible to carry out further anode bonding (Figure 2b). This can be explained by the surface tension of the glass. The height of the rise of the glass surface was 19.1-70.9 µm, and there was a tendency to increase the deformation of the glass with increasing temperature and annealing time. In the study of the dependence of the deformation on the annealing time, the onset of stationary equilibrium was recorded, in which the difference in glass deformation at 30 minutes and 60 minutes was minimal. This can be caused by a significant decrease in excess pressure during the formation of the spherical surface of the glass. In addition, at a temperature of 950 °C and prolonged annealing (more than 30 minutes), the formation of a crystallized film was observed on the glass surface, which significantly changes its properties. This limits the choice of temperature and annealing time.

![Figure 2](image_url)

Figure 2. Photo of samples after high-temperature annealing: 5 minutes of annealing time; (b) 2 minutes of annealing time.

Numerical modeling also showed the presence of glass deformation in the region above the cavity and the formation of a spherical profile (Figure 3). The calculation results show good agreement with the experimental results. Figures 4 (a, b) show the numerical and experimental results of the study of the development of glass deformation and changes in excess pressure in the time domain. The
obtained theoretical results of changes in the pressure difference between the environment and the chamber confirm the assumption of the onset of stationary equilibrium during a long annealing process. The creation of deeper cavities could increase the maximum deformation, but this requires the use of non-standard silicon substrates and longer plasma-chemical etching. The use of glass with a thinner thickness can also increase the maximum deformation, which confirmed by studies carried out on samples with thinned glass (Figure 4b). Thus, with a smaller diameter of the cavity, it was possible to achieve large deformations (71 μm). However, for this case, there is a greater discrepancy between the theoretical model and the experiment. It can be assumed that this is caused by the greater influence of the shrinkage of the glass during cooling due to the thinner glass wall. In addition, the choice of glass thickness is also limited by the thinning of the glass wall due to the elongation of the spherical profile. This is clearly seen in Figure 4 (a, b), where the change in the initial thickness Δh was 70 μm and 45 μm, respectively.

The difference between the upper and lower surfaces indicates an inhomogeneous thickness, which may be important for the use of this method in optics devices. The most promising way to increase the maximum deformation is to increase the initial pressure in the sealed cavity.

![Figure 3](image3.png)

**Figure 3.** Example of a deformation map with a cavity diameter of 750 microns, a glass thickness of 485 microns, and a heating time of 60 minutes.

![Figure 4](image4.png)

**Figure 4.** Theoretical and experimental results of studying glass deformation and pressure changes in the time domain: (a) cavity diameter 750 μm, glass thickness 485 μm; (b) cavity diameter 500 μm, glass thickness 200 μm.

On samples with a gold film deposited after annealing, glass deformation above the silicon cavity was also observed. For a cavity diameter of 500 μm, the lifting height of the upper surface was 48 μm, which corresponds to the theoretical results. After annealing, a change in the reflection spectrum was recorded, which indicates the presence of gold in the form of nanoparticles. In addition, a color gradient was observed in the area above the cavity. The EDS results show the presence of gold near the glass surface. The influence of this method of modifying the glass surface on the distribution of
nanoparticles was studied in areas close to air bubbles in the glass. These regions had a diameter of the deformed area of about 24 μm, which makes it possible to observe the change in the distribution of nanoparticles using SEM.

Figure 5 (a) shows the SEM image of a glass micro-bubble with a nanoparticle distribution. This image shows a change in the size of the nanoparticles and the distance between them; in the center of the deformed region, nanoparticles of the largest size (about 200 nm in diameter) were observed, and the array had the lowest density (Figure 5b). When moving away from the center, the size of the nanoparticles decreased to a diameter of about 75 μm.

**Figure 5.** SEM image of the glass surface with nano gold particles (a); area near the center of the formed bubble (b); area on the surface of the undeformed glass (c).

It is worth noting that despite the low adhesive force of gold nanoparticles to glass, mechanical action on the glass surface did not lead to the destruction of the nanoparticle array. It can be assumed that the nanoparticles were immersed in the glass after annealing.

4. Conclusion
The study shows the possibility of modifying the surface of LK-5 glass by glass blowing methods to solve the problems of manufacturing quantum frequency standards and ensuring a controlled distribution of metal nanoparticles on its surface. It is worth noting that the obtained results of glass deformation are significantly lower than the similar work using Pyrex glass [6]. An increase in
deformation can be achieved by optimizing the modes of the anode bonding to provide a greater residual pressure in the sealed cavity. Thus, the results of the work provide a broad basis for further research.

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