Single-step alkaline etching of deep silicon cavities for chip-scale atomic clock technology

I Komarevtsev$^{1,2}$, Y Akulshin$^{1}$ and A Kazakin$^{1,2}$

1 Peter the Great St Petersburg Polytechnic University, St Petersburg 195251, Russia
2 Alferov University, St Petersburg 194021, Russia

Abstract. This paper presents the results of experiments on the development of the technology of MEMS alkali vapor cells for a miniature quantum frequency standard. The classical design of a two-chamber silicon cell containing an optical chamber, shallow filtration channels and a technical container for a solid-state alkali source was implemented in a single-step process of wet anisotropic silicon etching. To prevent the destruction of the filtration channels during etching of the through silicon cavities, the shapes of the compensating structures at the convex corners of the silicon nitride mask were calculated and the composition of the silicon etchant was experimentally found. The experiments results were used in the manufacture of chip-scale atomic clock cells containing vapors of $^{87}\text{Rb}$ or $^{133}\text{Cs}$ isotopes in the neon atmosphere.

1. Introduction

During last few decades, deep alkaline silicon etching has been extensively used in the microelectromechanical systems (MEMS) industry. The anisotropic nature of silicon micromachining in organic and inorganic alkaline solutions is due to the significant difference in the dissolution rates of different facets of monocrystalline silicon [1,2]. Compared to deep vertical plasma etching of silicon, alkaline etching does not require expensive equipment and allows simultaneous processing of a large number of wafers. Therefore, it is preferred for the mass production of various MEMS containing bulk structures of a simple rectangular topology with a not high aspect ratio. These are pressure sensors, thermal sensors, accelerometers, microfluidics chips, etc. [3]. The same type of MEMS includes gas cells for chip-scale atomic clocks (CSAC) [4].

MEMS atomic cells containing alkali metal vapors are key elements of miniature optical-pumped quantum devices [5], such as magnetometers or frequency standards [6] used in satellite navigation [7]. The small size and energy consumption of CSAC operating on the effect of coherent population trapping (CPT) [8,9] are an undeniable advantage in this field. The atomic vapor cells are typically made of a silicon wafer sandwiched between two transparent borosilicate glass wafers. The main processes of the MEMS cells technology are through-wafer etching of silicon, filling with an alkali metal source and vacuum-tight sealing of the cell in the appropriate buffer atmosphere. Methods for sealing cells and filling them with alkali vapors are described in review [10]. Through-wafer dry or wet etching is used to form absorption cavities in silicon. Moreover, according to [9], it is desirable to use thick silicon substrates (500 – 1000 μm), since the depth of the cavities for optical probing plays an important role to determine the short-term relative frequency stability of CSAC.

The simplest cell designs contain a single absorption chamber, like the first cells produced by the NIST Company [4]. However, single-chamber cells require extremely precise dosing of a liquid or solid alkali metal source, since its excess leads to a violation of transparency. For this reason, for the mass production of CSAC two-chamber cell designs are used. Such cells consist of two sealed cavities...
with a volume of several cubic millimeters, connected by narrow filtration channels. One of the cavities is used to fill the cell with a solid alkali dispenser. The other contains only pure alkali metal vapors and an inert gas to provide optical absorption at a wavelength corresponding to the atomic line D1 of $^{133}\text{Cs}$, $^{85}\text{Rb}$ or $^{87}\text{Rb}$. Filtration channels provide, due to a small cross-section, a transfer of alkali atoms into the optical cavity without byproducts formed during laser activation of the dispenser [10].

The cells of the described design are mainly made by plasma etching of silicon [11]. Alkaline etching of silicon is excellent for single-chamber cells fabrication [9]. However, it is difficult to form compact two-chamber cells with an optical path length of about 1 mm by alkaline etching due to excessive undercutting at the convex corners of the mask, i.e. in places where the filtration channels connect to the cavities [12]. The formation of the internal volume of the cell by alkaline etching can be carried out in two stages to separately form through-wafer cavities and shallow channels. However, this way requires performing of several operations of deposition and removing of mask coatings, precise patterns alignment, and photolithography on the surface with deep relief.

To reduce the cost of atomic cells technology, a single-step alkaline etching for the simultaneous formation of through-wafer cavities and filtration channels has been developed. To reduce channel underetching, the appropriate etching solution has been experimentally determined and the designs of the mask topology with convex corners undercutting compensating structures have been developed.

2. Experimental details

The objects of the study were polished 3" silicon wafers with (100) orientation and thickness of 600 μm. 200 nm thick layer of silicon nitride was deposited on both sides of the wafer, and a mask pattern was formed on one side by direct photolithography and plasma etching. The mask pattern corresponded to the basic topology of two-chamber atomic cells with a total size of 6 x 6 x 1.6 mm (figure 1). The parameters of cells with $^{87}\text{Rb}$ vapors in the neon atmosphere at pressures of 200 – 400 Torr were calculated on the basis of preliminary experiments carried out in [13]. Their basic design contained two volumetric cavities with sizes of 3 x 1.5 x 0.6 mm, connected by rectangular channels with a length of 1 mm and a width of 100 or 200 μm.

Then, through-wafer etching of the cavities was carried out in tetramethyl ammonium hydroxide (TMAH) or potassium hydroxide (KOH) solutions at 80 °C for a time of about 6 – 10 hours (figure 2(a)). After mask removing, the wafers were used to make the cells as shown in figure 2.

![Figure 1. Two-chambers cell scheme.](image1)

![Figure 2. Cell fabrication process.](image2)

Depending on the etching conditions, the real appearance of the chips could differ from the basic design (figure 3). The etching rate and the distortion of the rectangular shape of the channels near the convex corners of the mask were measured using optical microscope and SEM (figure 4). For each
alkaline composition, at a fixed etching depth, the undercutting length \( l \) and the beveled angle \( \alpha \), i.e. an angle between the direction \([ml0]\) of maximum lateral undercutting and mask edges direction \([110]\), were measured. The beveled angle \( \alpha \) is a criterion for determining the Miller indexes of the \{mlk\} facets with the highest rate of dissolution in the etchant used [14]. The criterion of the relative rate of the convex corner undercutting is a dimensionless undercutting ratio \( U = l / h \), where \( h \) is the etching depth. These values were used to select the type and calculate the size of additional mask elements designed to compensate for the corner undercutting.

**Figure 3.** The \(^{87}\)Rb vapor cell, made by etching in 30\% KOH (Si chip size: 6 x 6 x 0.4 mm).

**Figure 4.** Convex corner undercutting.

### 3. Results and discussion

During anisotropic alkaline etching of (100) silicon surface through masks oriented in the <110> direction and containing rectangular holes with concave corners, through-wafer cavities or V-groove trenches with smooth walls inclined to the surface at an angle of 54.7° are formed, since they are limited by the (111) planes having an almost zero dissolution rate. When etching rectangular convex corners in silicon using anisotropic etchants such as TMAH or KOH, deformation of the edges always occurs (figure 4). This is due to the increased rate of dissolution of silicon facets with high Miller indexes (\{211\}, \{311\}, \{331\}, \{411\}, \{772\}, and etc.) with respect to the (100) surface. The specific facets that develop during convex corner undercutting depend on the composition of the etchant, its concentration, temperature, duration of etching, and the accuracy of matching the mask pattern with the [110] direction. For the two-chamber atomic cell design shown in figure 1, the convex corners of the mask are in places where the V-grooves channels connect to the through-wafer cavities. As a result, during the deep Si etching (> 400 \( \mu \)m) at normal conditions (30\% aqueous solution of KOH at 80 °C), the cell filtration channels with a length of 1 mm disappear and optical and dispenser cavities completely transform into one large cavity, as can be seen in figure 3.

But it is possible to compensate for the undercutting of convex corners by a suitable mask design. In the corner compensation method, extra features called compensating structures are added at all convex corners in the mask layout design to eliminate the deformation at convex corners during alkaline etching of silicon. Compensating structures of various geometries are used—triangle, square, <110>-oriented beam, <100>-oriented beam, superimposed squares and asymmetric beams and etc. (there are more than a dozen variants in total) [12]. Most types of known compensating structures are not suitable for the design of our cell geometry. The limited space for their placement in the cell cavities near narrow filtration channels does not allow the use of compensating structures in the form of triangle, <100>-oriented beam, superimposed squares and asymmetric beams. Only two variants of corners undercutting compensators can be chosen—<110>-oriented beam and square. The design of the nitride mask with these elements is shown in figure 5(a) and figure 6(a), respectively. Figures 5(b) and 6(b) show a compensation schemes for the fabrication of V-groove trenches connected to cell cavities. The dotted lines designate the shape of the structures as etching proceeds. The consumption of <110>-beam or square takes place by the initiation of undercutting at its convex corners. The evolving etched profile of compensation pattern clearly indicates that the significant beveling will take
place at the convex corners of channels. <110> beam type compensation design exhibits smaller beveling, depending on the beam’s width. For our design the width \( b \) was chosen to be 50 \( \mu \)m.

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** Mask design (a) and compensation scheme (b) for <110>-beam compensators. **Figure 6.** Mask design (a) and compensation scheme (b) for square compensators.

In order to determine the side length of such rectangular compensation geometries for etch depth \( h \), simple formulas can be derived using geometrical relations:

\[
L = Uh - 0.5b \cot \alpha \\
W = \frac{2Uh \sin \alpha}{2 \sin \alpha + \cos \alpha}
\]

(1)  (2)

Various parameters must be known for the analysis and the accurate design of the compensation geometry: etch rate of wafer surface plane \( (v_{100}) \); etch depth \( (h) \); undercutting length \( (l) \); beveled angle \( (\alpha) \); undercutting ratio: \( (U = l/h) \). These parameters strongly depend on the etching characteristics of the etchant and can only be found experimentally.

For the atomic cells fabrication, etchants based on aqueous solutions of KOH and TMAH of different concentrations were studied. Taking into account the large etching depth, the concentration of solutions in each group was selected to ensure the maximum rate and uniformity of (100) silicon surface dissolution. From this point of view, the best results were obtained with 30\% KOH and 15\% TMAH solutions. At 80 °C, the etching rates were 1.3 \( \mu \)m/min and 0.7 \( \mu \)m/min, respectively.

For both etchants, the value of convex corner undercutting was investigated and the directions of maximum lateral undercutting were determined. Figures 7(a) and 7(b) show the top views of the <110>-oriented beam structures etched in these etchants at 80 °C to the same depth of 18 \( \mu \)m. The values of beveled angle \( \alpha \), undercutting length \( l \) and ratio \( U \) and are given in table 1 in the corresponding columns. For both etchants, angle \( \alpha \) was close to 30.96 °. According to [14], it means that the maximum lateral undercutting occurs in the [410] direction, and the \{mlk\} facets developed during etching are \{441\} for 15\% TMAH and \{411\} for 30\% KOH [15,16]. By substituting the values \( U \) and \( \alpha \) in formulas 1 and 2, the length \( L \) of the <110>-oriented beam and side \( W \) of the square compensators, which are necessary to protect the channels during through-wafer etching of 600 \( \mu \)m thick substrate, was calculated. These values are shown in the last two columns of table 1. It is clear that TMAH etchant is not suitable for the manufacture of cells because the dimensions of both compensating structures exceed the width of the optical cavity or the distance between adjacent channels. In the case of KOH etchant, the compensating structures would occupy almost the entire space of the optical cavity. The huge size of the rectangular compensators for both etchants is due to the fact that the dissolution rates of the \{110\}, \{441\} and \{411\} facets exceed the etching rate of the (100) plane by one and a half or two times [2,16].
The view of convex corner undercutting in 15% TMAH (a), 30% KOH (b) and 30% KOH:IPA (c) solutions at 80 °C (beams width is 50 μm, etch depth is 18 μm).

**Table 1.** Etching parameters for calculating the size of rectangular compensating structures

| Etchant       | \( v_{100} \) (μm/min) | \( l \) (μm) | \( U = l / h \) | \( \alpha (°) \) | \{mlk\}  | \( L_{600} \) (μm) | \( W_{600} \) (μm) |
|---------------|-------------------------|--------------|-----------------|-----------------|---------|-------------------|-------------------|
| 15% TMAH      | 0.7                     | 75.4         | 4.19            | 29.9 ± 2        | \{441\} | 2470 ± 4          | 1345 ± 50         |
| 30% KOH       | 1.3                     | 45.4         | 2.52            | 30.7 ± 2        | \{411\} | 1470 ± 3          | 820 ± 30          |
| 30% KOH : IPA | 1.2                     | 23.1         | 1.28            | 25.3 ± 2        | \{331\} | 715 ± 5           | 370 ± 30          |

To reduce the rate of filtration channels undercutting, aqueous KOH solutions with additives of isopropyl alcohol (IPA) have been used. It is known that alcohol additives in KOH etchants reduce the rates of dissolution of the silicon facets with high Miller indexes [14,15]. The best results for the cells fabrication have been obtained with an etchant consisting of equal volumes of 30% aqueous KOH solution and IPA. Silicon etching has been carried out at a temperature of 80 °C in a container with a cooled lid to prevent the alcohol evaporation. The view of convex corner undercutting after etching under these conditions to a depth of 18 μm is shown in figure 7(c). The beveled angle \( \alpha \) is 25.3° ± 2°, which is close to the angle between [110] and [310] directions – 26.57° [14]. According to [15], it means that the facets developed during etching are {331}. The (100) plane etching rate in KOH:IPA etchant is 1.2 μm/min and it is comparable to the etching rate of aqueous KOH solution. But undercutting ratio \( U \) is two times less. The calculated average sizes of compensating structures were \( L = 715 \) μm and \( W = 370 \) μm for the <110>-beam and square types, respectively.

Using the ACES program, a simulation of the cell formation process in this etchant with a mask topology containing both of compensating structures was performed. For the simulation, the etching rate \( V_{100} \) from table 1 and the ratios \( V_{331}/V_{100} \) and \( V_{110}/V_{100} \) from [15] were used. For example, the etched silicon relief evolution when using a <110>- beam corner undercutting compensator is shown in figure 8. The achievement of the etching depth of 600 μm was determined by the complete closure of the (111) planes inside a square hole with a side \( a \) equal to 850 μm.

After making the appropriate photomask, KOH:IPA etchant was successfully used to fabricate one hundred atomic cells on a single silicon wafer. The optical cavities were etched through, the compensating structures were completely etched at the upper side of silicon relief, leaving the V-groove filtration channels open. However, there were distorted silicon ridges near the convex corners on the bottom side of the relief. It may be due to the development of additional facets during deep etching, which is difficult to simulate in the frame of simple model. To ensure that this phenomenon is not an obstacle to the normal operability of the atomic cells, the formation process was carried out with over-etching. The etching duration was increased to 11 hours, while the compensating structures size was increased to 1 mm for <110>-oriented beam and to 500 μm for square (while the distance between the channels was 700 μm). Figure 9 shows photos of the chips after the final stages of alkali vapor cell manufacturing – filling with a source of rubidium (or caesium) dispenser and anodic sealing.
with glass in a neon atmosphere. The suitability of cells manufactured using this technology for chip-scale atomic clocks was confirmed by appropriate tests [17].

**Figure 8.** Evolution of etched relief of cell cavity with <110>-beam compensators in 30% KOH:IPA etchant at 80 °C (a = 850 μm).

**Figure 9.** Cells made by etching in 30% KOH:IPA solution with the mask with compensators of the <110>-oriented beam (a) and square (b) types.

4. Conclusion
A method of single-step alkaline etching of silicon for fabrication of two-chamber MEMS atomic cells containing vapor of rubidium-87 or caesium-133 isotopes in a neon atmosphere was developed. To prevent the destruction of the filtration channels during etching of the through-wafer cavities, the <110>-oriented rectangular compensating structures at the convex corners of the silicon nitride mask were calculated and 30% KOH:IPA solution was used as silicon etchant. Developed technology is perspective for mass-production of chip-scale atomic clock.

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