Influence of electro-chemical etching parameters on the reflectance spectra of porous silicon rugate filters

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Abstract. Today the porous silicon photonic crystals are widely used as components of the optical sensors. The structures with the resonance properties, e.g. a narrow reflection band, which provides high sensitivity of the device, generate considerable interest. One of the most interesting structures of this type are rugate filters. Rugate filter is a photonic crystal with a gradually varying under harmonic law index of refraction and narrow spectral reflection band. In this paper, we present our results of the optimization of silicon electrochemical etching parameters, in order to fabricate filters in a visible spectral range with reflection bandwidth of less than 30 nm and a reflectance higher than 80%.

1. Introduction
Currently, optical sensors with fast response to the change of external conditions and high sensitivity are of interest. Special attention is drawn to the sensors based on photonic crystals (PhC), which provide the opportunity for management of the optical radiation [1]. One of the PhC type, for use in optical sensors application, is rugate filter [2], which have relatively narrow reflection spectrum in a contrast to conventional Bragg mirror. PhCs with sorption properties are of special interest, particularly porous silicon (pSi) photonic crystals have a large specific surface area [3] and branchy pore system. Photonic crystals based on pSi, including rugate filters, could be obtained by electro-chemical etching of silicon in aqueous-alcoholic solution of hydrofluoric acid [4]. The key optical characteristics of the fabricated samples depend on the etching parameters such as current density, current profile, etc. Frequently these relations are non-linear, thus an experimental selection of optimal etching parameters is required to obtain rugate filters with a narrow band and high reflectance.

2. Experiment
We used p-type silicon wafers with a resistivity of 0.003-0.005 Ohm-cm and surface orientation (100), manufactured by Telecom-STV, for the fabrication of rugate filters. Pure isopropyl alcohol, methanol and hydrogen peroxide were used for auxiliary operations during the sample production. Rugate filters based on porous silicon were fabricated using the standard technology of electro-chemical etching of monocrystalline silicon wafers. We took a water-alcohol solution of hydrofluoric acid (HF: C₂H₅OH - 1: 2). The etching current density varied in the range of 4-47 mA / cm². Current profile was sine-shaped in the vicinity of a base value. All silicon samples were pre-cleaned using ultrasound in isopropyl alcohol before etching and sequentially washed in methanol and hexane after. The final stage of rugate filters fabrication was their oxidation in solution of hydrogen peroxide to stabilize the surface chemical properties.
The etching of monocrystalline silicon was produced using programmable DC power KEITHLEY 2600A. Measurements of the reflectance spectra were carried out at the facility, which contained spectrometer OceanOptics USB2000+ with reflection fiber probe as the main element.

3. Results and discussion

To predict the optical parameters of manufactured rugate filters, it is necessary to determine the relation between the porosity value, and thus the structure refractive index, and parameters of the etching current. In order to solve this problem we made a series of porous silicon monolayer samples obtained with the use of different etching time and currents. Then, we measured mass of material removed in the etching process and the thickness of the porous layer for all the samples. To measure the mass of removed agents, each sample was weighed twice before and after etching. Measurement of the mass of samples was carried out using scales with an accuracy of 1 mg. In order to make sure that the electrolyte was completely removed from the porous layer after the etching we made the test weighing of pSi samples 3 days after the etching procedure. Control experiment showed similar results. The thicknesses of the porous layers were determined using SEM images of sample cross-sections, fig. 1. The obtained thickness of the etched layers allowed us to calculate the speed of sample etching and porosity at the different current settings. The porosity was calculated using the following equation:

$$P = \frac{m_1 - m_2}{\rho \cdot l \cdot S} \cdot 100\%,$$

where $m_1$ and $m_2$ - sample weights before and after etching respectively, $l$ - thickness of the porous layer, $S$ - etching surface area. The results are presented at Fig. 2.

![Figure 1. SEM images of the surface (left) and cross-section (right) of monolayer porous silicon obtained by etching current density of 4 (a) and 47 (b) mA/cm².](image)

The experimental results allow one to investigate the dependence of the effective refractive index on the value of PC etching current and link the etching time with the thickness of the resulting porous layer using the Bruggeman model [5]. Hence, it becomes possible to compare the results of theoretical modeling of rugate filters optical properties with the parameters of the experimental profile of the
etching current density. This principle has been realized with the use of transfer matrix method to calculate optical spectra of multilayer structures.

It is known [6], that the profile of the refractive index \( n \) in rugate filters varies sinusoidally. Therefore, each half-cycle of the \( n \) change was divided into 32 discrete elements in the theoretical modeling of reflectance spectra. Within each element \( n \) considered to be permanent.

![Figure 2. The dependence of the etch rate (left) and porosity (right) of the formed layer on the magnitude of the pSi etching current.](image)

The resulting model helped in optimization of the parameters of rugate filters based on pSi. Detailed calculations have been carried out for a filter with a reflectance spectrum maximum in the range of 550-650 nm. The first stage was the examination of the dependence of the rugate filters optical properties on the number of layers (periods) of the refractive index harmonic variations. A typical single layer thickness in this case was 160 nm for the mean value \( n = 1.8 \). It was found that a sharp increase in the maximum reflectance and narrowing of rugate filter spectral reflection band occurs as the number of layers \( N \) grows from 0 to 50. The significant improvement of the reflection profile shape and decrease of the secondary peaks amplitude of more than 25% was observed in the range of 50-100 number of structure layers (periods). Further layers number growth is not advisable, as it is not accompanied by a significant change in rugate filter parameters. Next, we investigated the effect of a smooth change in current density at the beginning and at the end of etching on the reflection spectra. This method theoretically allows one to reduce the difference in refractive index at the pSi/air boundary, which should lead to a further decrease of the secondary peaks intensity. The calculation results have confirmed this assumption and demonstrated reduction of the secondary peak amplitude more than a factor of \( 2 \), which corresponds to the literature data [6]. We placed extra emphasis on the dependence of the rugate filter reflection bandwidth on the amplitude change of the refractive index (etching current). Reducing of the amplitude modulation of the refractive index \( \Delta n \), as expected, resulted in the narrowing of the high-reflection bandwidth \( \Delta \lambda \), but the value of the reflection coefficient \( R \) decreased at the same time. However, as can be seen from Fig. 3 there is an optimal ratio between the values \( \Delta n \), \( \Delta \lambda \) and \( R \). Thereby, in case of rugate filter with a number of layers (periods) of the structure \( N = 100 \) and the mean value \( \langle n \rangle = 1.8 \) (which corresponds to the porosity of 62%) the optimal value of \( \Delta n \) is 0.05.
Figure 3. The dependence of rugate filter bandwidth (left) and its reflection (right) on the modulation of the refractive index values of \( n = \langle n \rangle \pm \Delta n \). The calculation was performed for rugate filter with \( \langle n \rangle = 1.8 \), single layer thickness (period) of 160 nm and the number of layers \( N = 100 \).

To examine our calculation we compared mathematical modeling results with experimentally measured reflection spectra for a series of rugate filter samples fabricated using different parameters for etching current. The calculated and experimentally measured reflection spectra of the rugate filter with a maximum reflectance at a wavelength of 615 nm represented as an example at Fig. 4.

Figure 4. Comparison of the calculated and experimentally measured reflection spectra of porous silicon rugate filter with the reflection spectrum peak wavelength of 615 nm. Etching current - 7.5 mA, etching current modulation - 1.5 mA, the thickness of a single rugate filter layer - 160 nm, the number of layers - 100.
It can be seen that the measured width of rugate filter equals 30 nm and is in a good agreement with the calculated value. The maximum reflectivity of experimental spectrum is lower than calculated one, but this fact is obviously caused by the defects in porous silicon structure and its absorption in the visible range. Furthermore, there is a significant shift between high reflectivity band position for measuring and calculated spectra, but this difference disappears when dispersion of refractive index is taken into account in calculation [7].

4. Conclusion
In this work we have investigated the dependence of reflectance spectra of the porous silicon rugate filters on electrochemical etching parameters. For silicon p-type KDB monocrystalline wafers with resistivity of 0.003-0.005 Ohm\cdot cm and a surface orientation (100), we measured the dependence of the porosity and the etching rate on the etching current density. We have demonstrated that the modeling of the optical properties of the pSi rugate filter in the visible range could be successfully performed using transfer matrices method and Bruggeman effective refractive index model. The calculation results allow us to optimize the etching process and fabricate rugate filters with maximum reflectance in a range of 550-650 nm, less than 30 nm bandwidth and a reflectance above 80%.

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