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Modification of optical properties of oxidised porous silicon by pore filling

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ABSTRACT

We report the experimental study of changes in optical properties of oxidised porous silicon induced by pore filling with salts from aqueous solutions. Our experiments demonstrate that pore filling is a simple and effective method for tuning the refractive index of porous silicon, which can be applied locally. This method can be used for creation of waveguides and other planar optical components. Our results correlate with previously reported works on the subject and provide information, which can be useful for the future investigation of porous materials.

Our samples were thin porous layers on top of Si wafers. We used aqueous solutions of several phosphate salts with various concentrations for filling the pores. After the pore filling, the dry samples were examined using optical spectrometry, microscopy (optical and electron) and EDS methods.

The paper provides description of the experimental procedures, data analysis and comparison with theoretical calculations.

1. Introduction

Porous silicon (PSi) is a metamaterial, which was discovered by A. Uhlir in 1956 [1]. Since then this material has been extensively studied because of its remarkable properties: porous silicon possesses extremely large surface area and high ability to absorb other substances in its pores, what makes it an attractive candidate for using in various fields ranging from optoelectronics to biomedical applications [2–6].

PSi is usually created by means of electrochemical etching of Si wafers, which results in formation of a porous layer on top of the wafer [7]. Thickness of the porous layer and pore diameter are determined by the etching current and time. Oxidation of PSi is commonly used to obtain environmental stability and hydrophilicity.

Diameter of the pores can be varied between several nanometres to several microns, depending on the Si resistivity and etching conditions. When the pore diameter is small compared to the wavelength of light, porous silicon can be used as an optical metamaterial. Optical properties of this material are determined by its structure and composition.

Porous silicon with specific index of refraction can be created by selecting appropriate parameters of the electrochemical etching and resistivity of Si. However, during the etching process the properties of the porous layer can be controlled only in the depth dimension. In order to create waveguides and other components lateral modifications are needed. Various methods of modification of refractive index of PSi have been reported, which employ focused proton beam or ion implantation [8,9].

Due to the ability of PSi to absorb foreign materials into the pores, this material is widely exploited as a chemical or biological sensor [10–16]. Absorption of material into the pores alters the composition of PSi and results in changes in its properties, which can be measured by optical means.

Void filling of porous silicon with various materials has been reported by several research groups. It has been demonstrated, that pores in silicon can be filled with liquids (water, acetone, ethanol and others), liquid crystals (5CB), polymers (PPV, polystyrene, polyvinylchloride), metals (Au, Ag, Cu, Ni) and other solids (e.g. NiO, TiO_2). The pore filling has been performed by means of various techniques: immersion, atomic layer deposition, chemical vapour deposition, sputtering and electrodeposition [17–30]. However, using salts to control optical properties of porous silicon has not been reported insofar.

Opposite to the common use of porous silicon as a sensor, in our work we study how optical properties of porous silicon can manipulated by intentionally altering its composition by pore filling. We have conducted several experiments in order to study the pore filling with aqueous salt solutions and to investigate the induced changes in the material's optical properties. Hydrogen phosphate salts were selected for the experiments for several reasons: these salts are transparent in the visible region, have good solubility in water and good wetting ability of the solutions, not hazardous and easy to work with. Besides, one of the salts used in our experiments (KDP) is commonly used as an

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optical non-linear material. We demonstrated that refractive index of porous silicon can be controlled locally by pore filling through a lithography mask.

We have found, that the process of pore filling with aqueous salt solutions, which we implemented, allows obtaining a composite material with modified optical properties and potentially can be used to adjust the index of refraction to desired values according to the needs. This process is simple and can be applied locally to create regions of high index of refraction, what makes is distinctive in comparison to other methods used for modification of refractive index of porous silicon. The effects of the pore filling were studied implementing different kinds of measurements: inspection under confocal and electron microscopes, energy-dispersive X-ray spectroscopy (EDS), and measurement of the reflection spectrum. In this paper we provide theoretical description of material properties of porous materials and of the pore filling process, detailed description of the experimental procedures and present the results accompanied by a discussion.

2. Theoretical background

The pores in PSi, which is produced from (100)-cut wafer, are oriented perpendicularly to the surface. In our case the diameter of the pores is of the order of 10 nm and the length is several microns. For light of wavelength, which is much larger than the pore diameter, i.e. 0.5 microns and longer, porous silicon behaves as bulk optical metamaterial. The specific pore orientation induces anisotropy in the bulk properties of the PSi.

To describe the refractive index of porous silicon we used the generalised Bruggeman model, which represents the effective susceptibility of a composite medium ε_{eff} by means of susceptibilities ε_i and volume fractions f_i of the composites and depolarisation factors L [31–33]. The effective susceptibility is calculated in this model according to formula:

$$\sum_i f_i \frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_{eff} + L(\varepsilon_i - \varepsilon_{eff})} = 0 \tag{1}$$

For porous silicon the depolarisation factors are $L_\perp = 1/2$ and $L_{||} = 0$, assuming cylindrical shape of the pores.

Oxidised porous silicon (OPSi) is described by this model as a composite medium consisting of SiO_2 and cylindrical voids. In case the oxidation in not complete, a fraction of Si should be considered as well. In OPSi with voids filled by some material, such as salt, the air is replaced by the filling material with the same volume fraction. In case of partial filling, the volume fraction of air is reduced and the remaining volume is occupied by the filling material. It is expected that pore filling will result in increase of the effective refraction index of OPSi.

OPSi layer of thickness of several microns etched on top of a Si wafer optically behaves as a thin film. Light reflection from such layer can be described by means of well-known formulae of thin film interference [34]. In the most general case, spectral reflection coefficient depends on angle of incidence and polarisation of the incoming light. Because of the anisotropic nature of OPSi, the effective refraction index for the light propagating inside the porous layer is also dependent on the angle of incidence. In the case of normal incidence, the refractive index of the light passing through the layer is the ordinary refractive index of OPSi.

The interfaces of the porous layer are not perfectly flat but possess a certain roughness, which affects the reflection coefficients at the layer interfaces and, consequently, the interference pattern. The effect of surface roughness on specular reflection coefficient at normal incidence can be taken in account according to formula [35]:

$$r_r = r \exp\left\{-\left(4\pi\frac{S_q}{\lambda}\right)^2\right\} \tag{2}$$

where r is the reflection coefficient of the smooth surface, S_q is RMS surface roughness and λ is wavelength. This results in the modification of the amplitude of the reflection coefficients r_{ij} at the surface interfaces between media with refractive indices n_i and n_j to the following form:

$$r_{ij} = \frac{n_i - n_j}{n_i + n_i} \exp\left\{-\left(4\pi\frac{S_{q,ij}}{\lambda}\right)^2\right\} \tag{3}$$

We obtain the salts inside the voids by means of treatment the OPSi with aqueous salt solution followed by drying. Pores of OPSi get filled with the solution by immersion of the sample or by placing a drop on the sample's surface. As the sample dries, the water evaporates, leaving dry salt inside the pores. It is expected, that salt crystallites will form on the pore walls during the drying process [36].

The process of filling the pores of oxidised porous silicon has been previously investigated [17,30]. To describe the filling of the pores with a liquid salt solution, the porous layer can be described as an assembly of capillaries, which are oriented perpendicularly to the surface [17]. It is assumed that the liquid can propagate only along the pore direction without cross-propagation between the pores. The filling with liquid is preceded by formation of a prewetting layer. The process penetration of the liquid into the pores can be explained by means of capillary filling, in which the driving force is Laplace pressure due to the surface tension of the liquid [17]. It is expected, that for a layer of pores of diameter between 10 and 20 nm and thickness of about 10 microns the process of filling with a liquid occurs within tens of milliseconds [17]. Since the amount of salt contained in solution is limited by the saturation concentration, the pore filling is expected to be incomplete [36]. Pore filling may also be affected by air, which may remain in the pores during the filling process [17].

3. Description of the experiments

Several experiments were performed in order to investigate the penetration of the liquid salt solutions into the pores and the influence of immersion time and salt concentration on the layer's refraction index and the surface roughness. The samples, which were used in the experiments, were pieces of silicon wafers with thin layers of oxidised porous silicon created on top of them. Several experiments were conducted, in which the samples were treated with liquid salt solutions followed by drying. All experiments were conducted in room conditions in laboratory environment.

The pore filling was achieved by immersion of the samples completely into the liquids or by placing liquid drops on their surface. Nitrogen gas flow and spinner P7600 from Specialty Coating Systems were used to remove the excess liquid and dry the samples. The spinner was operated at 3000 rpm for 100 s. It was essential to remove the excess liquid from a sample's surface and perform fast drying in order to avoid formation of salt crystallites on the surface. Drying the samples with the spinner provided better uniformity of the dry surface in comparison to drying with the nitrogen flow.

The experiments were performed with several kinds of OPSi samples. Part of the experiments was performed using samples produced by SiLiMiXT Company (France), while the rest of the experiments was performed with OPSi samples created in our laboratories at Tel-Aviv University (TAU). All the samples were fabricated from p-type silicon wafers with (100) orientation. In the OPSi samples from SiLiMiXT the thickness of the porous layer was 5 microns ± 10% and the pore diameter was about 20 nm. The OPSi samples created at TAU had porous layer of thickness 7–8 microns and pores of diameter about 15 nm. In TAU the porous layers were fabricated by electrochemical etching of p-type Si wafers with resistivity of 0.01–0.02 Ohm·cm. The etching took place in a mixture of HF (48%) with C_2H_5OH in proportion 1:1 by volume at current densities 30 mA/cm^2 and 50 mA/cm^2 at various etching times. All the samples were thermally oxidised using a two-step process: preoxidation at 300 °C for 30 min followed by oxidation at 900 °C for 2 h. The oxidation was necessary in order to environmentally stabilise the samples and to ensure their hydrophilicity. SEM images of