thin solid films

Visual determination of thickness and porosity of porous silicon layers

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Abstract

Optical characteristics of porous silicon layers of different thickness and porosity are simulated and interference spectra are calculated. The results are presented as curves on a colorimetric diagram. For thicknesses up to 500 nm, analysis of colors has shown that the interference color is directly related to the product of thickness and porosity of porous silicon layer. Practical techniques, which enable one to visually define thickness (or porosity) of a porous silicon layer at known porosity (or thickness), are developed. The method has high accuracy and is easy to use, it does not need destruction of the sample and allows one to make the control in selected local areas. A similar technique is useful for in-situ analysis during the porous silicon anodization process. The method applied to dried porous structures and those filled by water allows determination of both thickness and porosity of a porous silicon layer at one time. © 1997 Elsevier Science S.A.

Keywords: Porosity; Thickness; Silicon; Optical properties

1. Introduction

The structuring of materials at the nanometre level changes their fundamental properties and opens new opportunities for applications. Chemical and electrochemical methods of nanostructuring can be used on silicon. One of the most actively researched nanostructured material is porous silicon (PS), which can be formed by anodic processing of crystalline silicon in HF acid solutions [1]. During the formation of the porous structure in monocrystalline silicon the long-range atomic ordering is preserved: this results in specific properties of this porous material. Some of the properties, connected with luminescence in the visible range [2], are a subject of intensive research [3,4].

PS layers can be characterised by a large number of parameters, nevertheless the thickness, d, and the porosity, p, are the principal ones. The standard technique for thickness evaluation consists of local removal of a part of the layer (for example by mechanical treatment or by chemical etching) and optical (or cross-sectional scanning electron microscopy

(SEM)) measurement of the step size. The achievable accuracy (~ 0.05 μm) is sufficient for the majority of scientific and technical measurements. For porosity measurement the gravimetric method is generally used: the change in weight of the substrate before and after the anodization process is measured by a precision balance. By knowing the PS layer thickness and area it is possible to calculate it's specific weight and porosity. Accuracy of this method is rather low: at a layer thickness of ~ 200 nm and area of the removed part of ~ 1 cm^2 with accuracy of weighting ~ 50 μg, the error in porosity determination can easily reach 100%.

The described methods of measurements are complicated and destructive. Moreover they are not useful for in-situ parameter evaluation during the PS formation. In this paper an innovative technique is introduced. This method allows the evaluation of the PS layers parameters by observing interference colours in a way similar to the known techniques used in everyday laboratory practice for transparent layers of SiO$_2$, Si$_3$N$_4$. As the interference colour is subjected to changes due to both thickness and porosity, the authors introduce an integrated parameter, which determines the interference colour. The use of this parameter allows one to quickly and rather precisely calculate porosity of a PS layer with known thick-

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ness. In addition a more complex technique is introduced, which by filling the porous layer by liquid, allows one to define thickness and porosity of PS layers simultaneously.

2. Optical characteristics of porous silicon

In Fig. 1 spectral dependencies of experimentally measured real and imaginary parts ($Re(n)$ and $Im(n)$) of the monocrystalline silicon refractive index [5], and the calculated ones for PS modelled with spherical ($Re(n_0)$ and $Im(n_0)$) and cylindrical ($Re(n_1)$ and $Im(n_1)$) pores (50% porosity for both the cases) are shown.

The refractive index of porous silicon can be calculated from the expressions for the local electric field of a light wave in a medium consisting of cylindrical (E_1) or spherical (E_0) pores filled by a substance of dielectric constant ϵ_m [6]:

$$E_0 = \frac{3\epsilon}{2\epsilon + \epsilon_m} E \tag{1}$$

$$E_1 = \frac{2\epsilon}{\epsilon + \epsilon_m} E \tag{2}$$

where E and ϵ are the electric field and the dielectric constant in the homogeneous medium, respectively. For cylindrical pores the electric field has been assumed perpendicular to the cylinder axis.

From geometric considerations, a first-order description of the macroscopic electric field (E_A) and of the total energy carried by the field W_A can be separated into two contributions due to the field in the pores (E_0) and in the surrounding material E:

$$E_A = pE_0 + (1-p)E \tag{3}$$

$$W_A = p\epsilon_m\epsilon_0\frac{E_0^2}{2} + (1-p)\epsilon\epsilon_0\frac{E^2}{2} \tag{4}$$

At the same time, introducing an equivalent, macroscopic, dielectric constant ϵ_{A0}, the energy density can be expressed as:

$$W_A = \epsilon_{A0}\epsilon_0\frac{E_A^2}{2} \tag{5}$$

By comparing expressions 1 to 5, it is possible to obtain expressions for ϵ_{A0}, ϵ_{A1} (for spherical and cylindrical pores respectively), and after transforming the equations by changing parameters from dielectric constants to refractive indexes,

$$n_0 = n\frac{\sqrt{(5p+4)(nn_m)^2 + (n_m^4 + 4n^4)(1-p)}}{(2+p)n^2 + (1-p)n_m^2} \tag{6}$$

$$n_1 = n\frac{\sqrt{(2p+2)(nn_m)^2 + (n_m^4 + n^4)(1-p)}}{(1+p)n^2 + (1-p)n_m^2} \tag{7}$$

It should be noted that by air filling of pores $n_m = 1$, whereas by water filling of pores $n_m = 1.33$. Fig. 1 shows that PS morphology influences optical properties, but even the most significant changes of structure (spheres or cylinders) does not result in sizeable differences. Hereinafter all calculations are carried out using the cylindrical pores model.
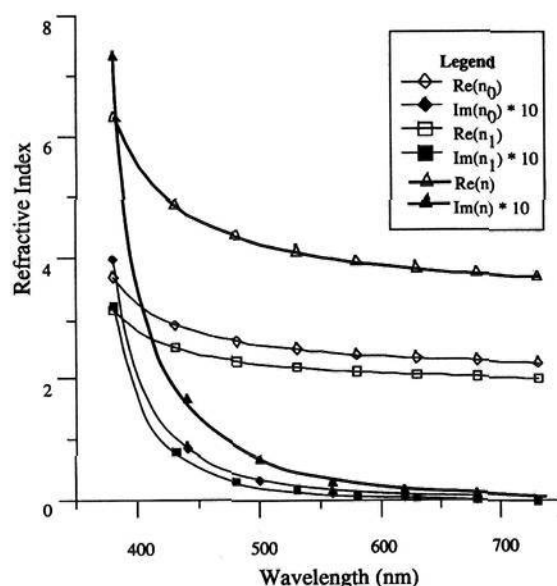
3. Spectral dependence of reflection from porous silicon layers

In Fig. 2 the beams which form interference colour in case of normal incident light are shown. Reflection due to the difference of refractive indexes is described by the known expression based on Fresnel's formulas, in which d is the film thickness, λ the wavelength, n_m, n_1 and n respectively the refractive index of the pore medium, PS layer and bulk silicon:

Fig. 1. Real and imaginary parts of the refractive index of monocrystalline and porous silicon as a function of the wavelength. $Re(n)$ and $Im(n)$ represent the experimentally measured real and imaginary parts of the monocrystalline silicon refractive index; $Re(n_o)$, $Im(n_o)$ and $Re(n_1)$ and $Im(n_1)$ are the calculated real and imaginary parts of PS assuming respectively spherical and cylindrical pores (50% porosity in both cases).
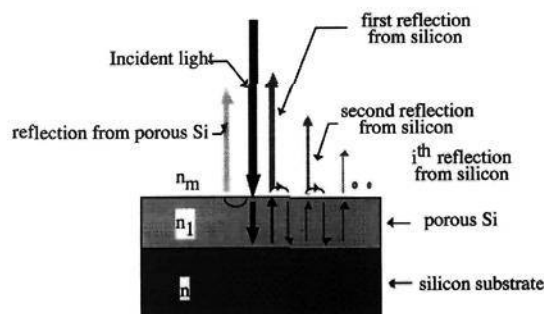

Fig. 2. Origin of the colour exhibited by porous silicon layers by interference of light reflected at the interfaces.

$$R = \left| \frac{R_{1-2} + R_{2-3} \exp\left(\dfrac{4\pi i n_1 d}{\lambda}\right)}{1 + R_{1-2} \cdot R_{2-3} \exp\left(\dfrac{4\pi i n_1 d}{\lambda}\right)} \right|^2 \qquad (8)$$

$$R_{1-2} = \frac{n_1 - n_m}{n_1 + n_m} \qquad (9)$$

$$R_{2-3} = \frac{n - n_1}{n + n_1} \qquad (10)$$

The reflection coefficient R depends on the wavelength and it is this dependence that give rise to the colour of PS layers.

4. Colour coordinates

For objective evaluation and representation of colour we used the XYZ colour coordinate system proposed by the International Commission of Illumination [7]. In Fig. 3 a representation of colours on an XY flat (in this case $Z = 1 - X - Y$) are shown. In the same figure the spectral locus and colour triangle for CRT monitors are also presented [7].

It is possible to note that at small layer thicknesses PS colours vary from yellow up to blue–purple; as the thickness increases further the colours change moving on the green–red line, monotonically decreasing the colour depth.

5. Definition of thickness (porosity) of porous silicon layers

In Fig. 4 a subset of the data shown in Fig. 3 is plotted as a function of the thickness of the PS layer. The reported value is the angle (in degrees) of the vector describing the spiral.
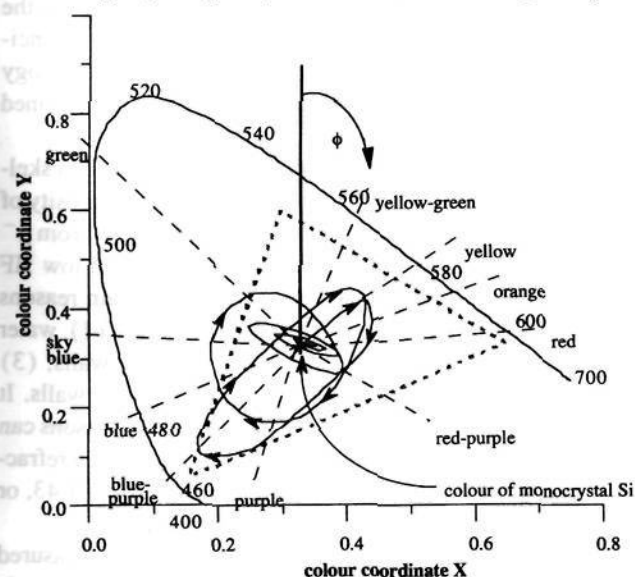
Fig. 3. Spectral locus exhibited by a porous silicon layer (porosity = 75%) as a function of its thickness in the range 0–1500 nm (solid spiral). In addition the colour triangle for CRT monitor is reported (dashed line).
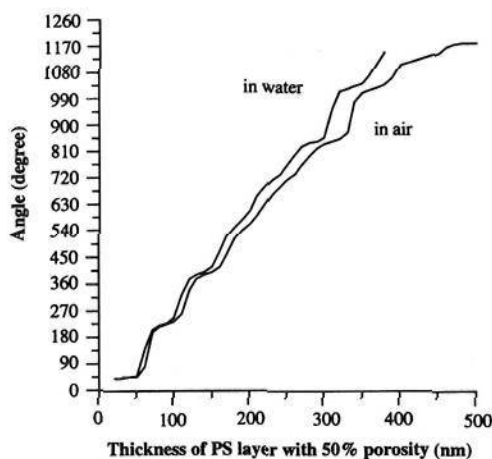
Fig. 4. Angle of spiral (in degrees) in Fig. 3 as a function of the thickness of PS layer.

The colour of monocrystalline silicon is in the centre of the spiral, the thickness (with porosity 50%) is limited to 500 nm, in order to work with the brightest and saturated colours.

The elliptic shape of the spiral results in steps of angle-thickness dependence. It is possible to identify areas (e.g. thickness 335 nm at 50% porosity) in which even insignificant changes of thickness or porosity result in sharp colour change, and others where even significant changes of the same parameters do not affect colouring (e.g. thickness 365 nm at 50% porosity). On the average a 100 nm change of thickness causes a 300° change of the angle.

The directions of main colour shades in Fig. 3 allow one to locate the angle with an accuracy of $\pm 20°$, which corresponds to accuracy of measurement of thickness of approximately 7 nm at $p = 50\%$.

To evaluate the influence of porosity on colouring, the appropriate refractive index dependence has been analysed and the results are indicated in Fig. 5. In the figure the dependence of PS relative refractive index with respect to 50% porosity PS refractive index is reported for different wavelengths. The lines do not coincide completely: changing the porosity an additional dispersion appears which is more appreciable in the dark blue part of the spectral range; however the distinction is not significant.

The colour is determined by the film optical thickness, therefore to estimate the thickness and porosity of a PS layer further calculations are required as follows. The thickness of a 50% porosity film, $d_{(50\%)}$, is evaluated starting from the colour of the sample which is used to determine the spiral angle ϕ (Fig. 3). ϕ is then used in Fig. 4 to obtain $d_{(50\%)}$. Then,

1. if the thickness of the film is known (e.g. by results of measurements on cleaved samples), the relative refractive index is calculated as the ratio between the effective thickness $d_{(50\%)}$ and the measured one, and then by using Fig. 5(a) the unknown porosity is determined;
2. if porosity (and thus relative refractive index of the film) is known, the unknown thickness is evaluated as the ratio between effective thickness and relative refractive index.
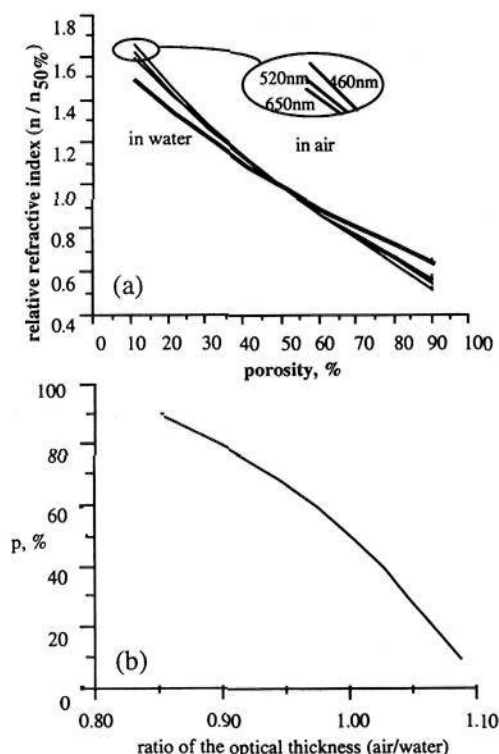
Fig. 5. (a) Effective refractive index as a function of porosity for PS filled by water and by air (450, 550 and 650 nm). (b) Porosity as a function of ratio between the effective optical thickness determined when PS is filled by air and by water.

6. Definition of PS layer thickness directly in the anodization process

The interference colour changes are observed during immersion of a PS structure in liquid solutions. The observed change of colour is due to pores filling with a liquid of refractive index higher than 1 (air) and consequent increase of optical thickness.

The presence of a thin oxide layer formed on the porous structure just after some minutes of air exposition has been neglected in the calculation of the optical thickness. In Figs. 4 and 5(a) the plots needed to define the thickness or porosity of water-immersed layers are presented.

Since during the anodization process the PS layer is often immersed in a primarily aqueous solution, the considered technique can be effectively applied to control the process. In particular, it is possible to quantitatively monitor the local inhomogeneity of PS layer's thickness.

7. Visual definition of thickness and porosity of porous silicon layers

Differences in the refractive index of the substance used for filling the pores (e.g. water and air) results in a different relative refractive index of the layer (in Fig. 5(a) the curves have different slope). The optical thickness of a layer is the product of thickness and refractive index. Accordingly, for

the same thickness two different optical thicknesses should be measured in air and in water. As a consequence, it is possible to define the porosity of a PS layer by comparing the optical thicknesses in water and in air. Fig. 5(b) reports calculated porosity as a function of the ratio between optical thickness measured in air and water. Having determined porosity, the thickness of the PS layer can be calculated by using the technique described in the previous sections.

The accuracy of this method is rather low, but it is still suitable for diagnostic purposes. To improve the accuracy it is possible to use a liquid with higher refractive index, but this is not convenient from a practical point of view.

8. Comparison with experimental results

Since the determination of the interference colour from the layer with known refractive index is an unequivocally soluble physical problem, the actual distinctions between theoretical and experimental results can be connected only to deviations from assumptions used for the refractive index calculation. Such assumptions are: (1) cylindrical morphology of the porous silicon structure; (2) the remaining silicon skeleton has the same refractive index as monocrystalline silicon. The presence of oxide on the pore surface can be taken into account to improve the model.

The assumption about cylindrical morphology of porous silicon seems to match rather closely the real structure. The refractive index values [6] measured by the ellipsometric method (angle of incident beam, −70°) are appreciably lower (about 4–8%) than the values measured by reflection (at normal incident beam). Within the framework of the model considered in Ref. [6] with spherical morphology the refractive index should be independent of the angle of incident beam; nevertheless, assuming a cylindrical morphology the experimentally observable difference is easily explained by anisotropy of PS optical properties.

The refractive index change of the remaining silicon skeleton can be observed at small pores size and high porosity of the structure. Such a type of structure usually results from p^- silicon substrates under high current densities and low HF concentration electrochemical treatment. The main reasons causing the change of the refractive index are: (1) water adsorption in micropores; (2) oxidation of pore walls; (3) amorphisation of monocrystalline silicon at pores walls. It should be noted that the effect from the first two reasons can be reduced by measurements in water or liquid with a refractive index similar to SiO_2 (e.g. ethylene glycol, $n = 1.43$, or glycerine, $n = 1.47$).

In Fig. 6 the plot of conformity of PS densities measured by the gravimetric method and by the presented technique is shown. This plot is constructed using data from Ref. [8], which are recalculated for cylindrical porous morphology.
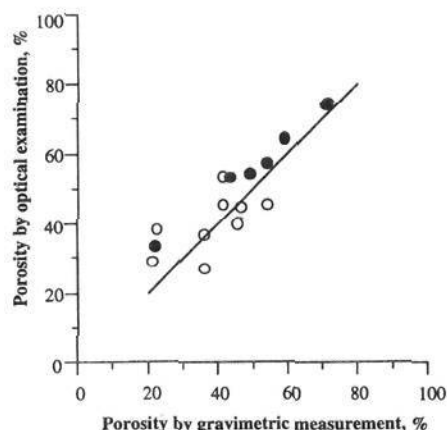
Fig. 6. Comparison of optically and gravimetrically determined porosity for PS samples (●, 0.01 Ω cm; ○, 25 Ω cm starting substrates).

9. Conclusions

In this paper a new quantitative method for the determination of porous silicon layer thickness and porosity is presented. The non-destructive and easy to implement method is being based on the visual comparison of interference colours showed by PS layers when filled by different substances (e.g. air, water).

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