Linear and Nonlinear Optical Characteristics of Porous Silicon

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The susceptibility of the model medium consistinf of identical and parallelly oriented columns (wires) was considered by use of the generalized method of the integral rquations (MIE). Such a model resembles mesostructure of the porous silicon (PS) samples. For a given mesostructure the optical anisotropy is closely connected with the porosity of the medium. We predict a great anisotropy of tlic PS nonlinear susceptibility tensor.

I. Introduction

The discovery of efficient photoluminescence of highly porous silicon (PS) in a visible range at room temperature[1] has generated a great interest in this material in view of its possible use for optoelectronic applications. The attribution of this luminescence to quantum-confined carriers in crystalline Si columns (wires) has been supported by direct transmission electron microscopy measurements.[2] The detected optical anisotropy of the PS samples under optical reflectometry investigations[3] also validates this claim. Thus the concept that the microstructure of highly porous silicon can be characterized by an array of tiny (as narrow as several nm) Si columns, in which the crystalline order is preserved, is now widely accepted.

From the optical viewpoint, such an unusual PS micromorphology with the sizes larger than the interatomic ones but much less than wavelength creats a problem of finding a proper approach for calculation of its optical properties. When the distances between columns are of the same order as their diameters, we may be sure that local field effects foi linear and nonlinear susceptibilities will play the prominent role. The method of integral equations (MIE) is the unique approach for exact allowance of all these effects and calculation of macroscopic susceptibilities of a medium with any microstructure. But MIE has never been applied to two-dimensional mesostructural media. Here we are developing tlie general MIE approach[4] for planar systems. The mesoscopic effects of PS structure are taken into account by means of the concept of a mesoscopic "elementary radiator" - dielectric cylinder. MIE together with this new concept allows us to calculate a susceptibility of porous silicon with arbitrary porosity. The basis for two-dimensional consideration of PS films leans on the fact that their properties in a vertical direction are more or less uniform. For the limiting cases of high and small porosity, our results coincide with the formulae (9), (10) of ref. [3], which were obtained by perturbation theory when local field effects are neglected. Investigation of the optical properties of PS films, in particular an optical anisotropy, gives valuable information about porosity of the material and permits some conclusions about the connection of the photoluminescence spectra with the nanostructiire of the porous silicon. Since the optical properties of the two-dimensional systeins may strikingly differ from the three-dimensional ones, we cite here the results of the MIE application to this special case.

II. MIE for planar systems

By analogy witli the 3D-case[4], in the 2D-case the "two-dimensional dipole" (i.e. double charge string)

may be written in the form

$$\vec{E} = \pi i k \frac{L^{(1)}}{R}[2\vec{n}(\vec{n}\cdot\vec{d}) - \vec{d}] + \pi i k^2 H_0^{(1)}[\vec{d} - \vec{n}(\vec{n}\cdot\vec{d})]$$

$$H_z = -\pi k^2 H_1^{(1)}\vec{n}\cdot\vec{d}\cdot\vec{E} \equiv (E_x, E_y, 0) \qquad (1)$$

For E_z-component of the electric field and planar vector $\vec{H} = (H_x, H_y, 0)$ there are the relationships

$$E_z = \pi i k^2 H_0^{(1)} d_z, \quad \vec{H} = -i\pi k^2 H_1^{(1)}\hat{\sigma}_y \cdot \vec{n} d_z , \qquad (2a)$$

where $H_0^{(1)}$ and $H_0^{(1)}$ are the Hankel functions of the first kind, $\vec{n}$ is the unit vector in the x, y plane, and $\vec{R} = \vec{r} - \vec{r}'; \vec{n} = \vec{R}/R$. The two-dimensional vectors $\vec{r}'$ and $\vec{r}$ describe position of a dipole and the observation point, respectively; $\vec{d}$ is the linear density of the dipole moment, $k = \omega/c$ is the wavenumber, and $\hat{\sigma}_y$ is the Pauli y-matrix:

$$\hat{\sigma} = \begin{pmatrix} 0 & i \\ -i & 0 \end{pmatrix} \qquad (2b)$$

Using Eqs. (1-2) we may construct the integral equation in just the same manner as in the 3D-case:

$$\vec{E}' = \vec{E}_i + \vec{E}_\sigma + \int \nabla \times \nabla \times \vec{P}G d^3\vec{r} , \qquad (3)$$

where $\vec{E}_i$ is the incident field, $\vec{E}_\sigma$ is the field of the dipoles inside the Lorentz "two- dimensional sphere" (cylinder), $\vec{P}$ is the volume density of the dipole moment, and $G = \pi i H_0^{(1)}(kR)$ is the Green function of a two-dimensional wave equation.

By use of the substitution of variables[4] proposed earlier, which corresponds to the passage from microscopical field $\vec{E}'$ to the new variable-field $\vec{E}$, the following relation may be written:

$$\vec{E} = \vec{E}' + \hat{\beta} \cdot \vec{P} , \qquad (3)$$

where $\hat{\beta}$ is an arbitrary tensor of the second rank. If one tries to connect the newly introduced quantity $\vec{E}$ with any measurements of the electric field inside the medium, it becomes evident that in a general case tensor $\hat{\beta}$ would depend both on the properties of the separate radiators and the microstructure of the medium.

Let us impose a physical constraint on this new variable $\vec{E}$ by the requirement that, in addition to the integral equation, it must satisfy the wave equation as well

$$\nabla \times \nabla \times \vec{E}k^2\vec{E} = -4\pi k^2\vec{P} . \qquad (4)$$

Then it may be shown that Eqs. (3) and (4) together impose on the tensor 3 quite a definite limitation so that it may depend on the microstructure of the medium only. For the given polarizability of a separate radiator, the tensor $\hat{\beta}$ totally determines all optical properties of the medium, in particular the dielectric permittivity i. In the case of the three-dimensional chaotic or cubic lattice, this tensor has the form

$$\beta = \begin{pmatrix} -\frac{4\pi}{3} & 0 & 0 \\ 0 & -\frac{4\pi}{3} & 0 \\ 0 & 0 & -\frac{4\pi}{3} \end{pmatrix} . \qquad (5)$$

I-i the considered 2D-case of infinitely long "dipole threads" oriented along the z-axis and disposed in the x, y plane chaotically or in a quadratic lattice manner, the tensor $\hat{\beta}$ takes the form

$$\hat{\beta} = \begin{pmatrix} -2\pi & 0 & 0 \\ 0 & -2\pi & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (6)$$

III. The choice of the "elementary radiator"

The peculiarity of the porous silicon microstructure lies in the intermediate (between the interatomic distances a and wavelength A) characteristic size, i.e., cylinder's diameter D: $a << D << \lambda$. Inside the cylinders atoms may be considered as arranged in the regular manner, but the cylinders, are disposed accidentally. Therefore, we come to the problem of nonuniform distribution of atoms inside Lorentz sphere, i.e. a spatially nonuniform problem. For any type of micromorphology of the medium it leads to great mathematical difficulties. In order to avoid these difficulties, we take advantage of the fact that just a.s a. sphere in a uniform electric field gives rise to an exact dipole radiation, in the external uniform field the radiation from a dielectric cylinder of an arbitrary radius coincides with the "plane

dipole" field[5]. *Then we may choose such a cylinder as an elementary radiator ("atom") and apply the MIE for a collection of such chaotically disposed radiators.*

Under chaotic distribution of the cylinders the uniform electric field in the region of the Lorentz cavity's center appears. As a result, we can consider the medium as if it would be constructed not from cylinders but from thin threads. Therefore we may apply Eq. (1). For obtaining the solution, it is necessary to determine the polarizability of each cylinder.

IV. Application of the method to the PS-type structure

Using the known solution for the cylinder in a uniform field,[5] we have for the polarizability tensor α : ($\vec{P} = N\hat{\alpha}E$) the following expressions:

$$\hat{\alpha} = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

$$\alpha_{xx} = \alpha_{yy} = \frac{1}{2}\frac{\epsilon-1}{\epsilon+1}r_0^2, \tag{7}$$

$$\alpha_{zz} = \frac{\epsilon-1}{4}r_0^2 .$$

The components of the dielectric permittivity tensor $\vec{\epsilon}$ are connected with the tensor α components by the relations

$$\hat{\epsilon} - 1 = 4\pi N\hat{\alpha} \cdot (1 + 4\pi\beta \cdot N\hat{\alpha})^{-1} \tag{8}$$

$$\epsilon_{xx} = \epsilon_{yy} = \frac{\epsilon+1+c(\epsilon-1)}{\epsilon+1-c(\epsilon-1)},$$

$$\epsilon_{zz} - 1 = c(\epsilon-1).$$

where N is the density of the cylinders in 'LU-case and the spheres in 3D-case, ϵ is the dielectric permittivity of the volume material, and $c = \pi r_0^2 N$ is the bulk material concentration.

For description of the optical properties of the film it is convenient to introduce the optical anisotropy parameter

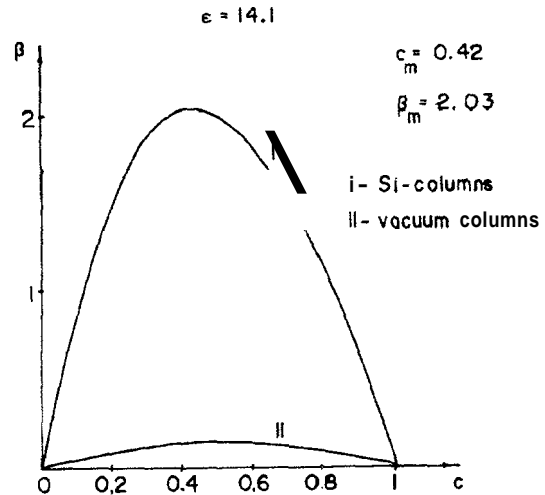$$\beta = \frac{\epsilon_{zz}}{\epsilon_{xx}} - 1 . \tag{9}$$

Figure 1: The optical anisotropy dependence vs concentration of silicon V in the case of silicon columns.

Then from (8) and (9), we obtain

$$\beta = c(1-c)\frac{(\epsilon-1)^2}{\epsilon+1+c(\epsilon-1)} . \tag{10}$$

For small concentrations $(c \ll 1)$, Eq. (10) coincides with the results of Ref. [3]

$$\beta = c\frac{(\epsilon-1)^2}{\epsilon+1} . \tag{11}$$

which holds when the influence of the dielectric columns on each other is not taken into account. (When introduced in such a way an anisotropy parameter β is connected with the anisotropy parameter $\tilde{\beta}$ of the Ref [3] by the relation $\beta - 1 = (\tilde{\beta} - 1)^2$).

For large bulk material concentration $|1 - c| \ll 1$ Eq. (10) takes the form

$$\beta = (1 - c)\frac{(\epsilon-1)^2}{2\epsilon} . \tag{12}$$

In both of the limit cases, β naturally turns to zero for homogeneous one-component media

The optical anisotropy dependence vs concentration c is shown in Fig. 1

The maximum value of an anisotropy is

$$\beta_m = (\sqrt{2\epsilon} - \sqrt{\epsilon+1})^2 \tag{13}$$

at the concentration

$$c_m = \sqrt{\frac{\epsilon+1}{\epsilon-1}} (\sqrt{2\epsilon} - \sqrt{\epsilon+1}) \tag{14}$$

From (14) it follows that $c_m < 0.5$ for any ϵ. With $\epsilon \to \infty$, c, acquires the lower limit $C_{max} = \sqrt{2} - 1 \simeq 0.41$. This shift and assymetry of the $\beta(c)$-dependence is the manifestation of the elongated column-like morphology of the porous silicon. For any "symmetrical" (relative to the transformation vacuum $\leftrightarrow$ dielectric) form of inclusions, anisotropy β will be maximal at $c = 0.5$.

Perhaps the question may arise: how is it possible to obtain large concentrations c (more than the limit concentration $c_c = \frac{\pi}{\sqrt{12}} \simeq 0.90$ for the close packing of the identical cylinders)? The answer lies in the mesoscopic cylinders treatment as elementary radiating "threads" which in fac. takes into account their possible "over-lappings". I ysically these overlappings mean twofold enhancement of the dielectric permittivity in the over-lapped area. Therefore, the formulae hold true up to $c = 1$.

It is possible to calculate the dielectric permittivity of a set of the vacuum columns in the crystalline silicon. For this it is necessary to perform a substitution $1 - c$ for c and ϵ^{-1} for ϵ (the last follows from the fact that in these equations really enters the ratio of the fractions' permittivities).

As a result we obtain

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon \frac{2 + c(\epsilon - 1)}{2\epsilon - c(\epsilon - 1)}, \quad \epsilon_{zz} = \epsilon - (1 - c)(\epsilon - 1) \tag{15}$$

where c is the concentration of the crystalline silicon.

Fig. 2 shows how the anisotropy β depends on the silicon concentration in this case. This dependence is critically distinct from that shown in Fig. 1. The maximum value of the anisotropy is:

$$1 - c_m = \frac{\sqrt{\epsilon + 1}}{\epsilon - 1}(\sqrt{2\epsilon} - \sqrt{\epsilon - 1}) \tag{16}$$

$$\beta_m = \frac{(\sqrt{2\epsilon} - \sqrt{\epsilon + 1})^2}{\epsilon} \tag{17}$$

and for large $\epsilon \gg 1$ this value is ϵ times less than for the silicon columns-type geometry.
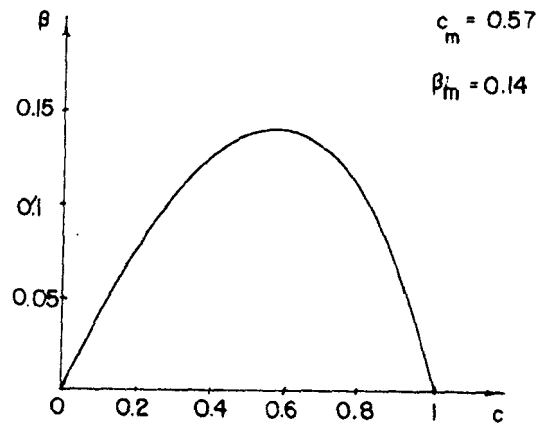

Figure 2: The optical anisotropy dependence vs concentration of silicon c in the case of vacuum columns.

Thus, these examples vividly demonstrate that the macroscopic optical properties of the composite system depend dramatically not only on the concentration of the material but on the form of the inclusions as well.

V. Nonlinear properties of PS

The foregoing consideration allows definite conclusions about PS nonlinear optical characteistics. Firstly, all the nonlinear sources in the right-hand part of the wave equation will differ from the respective nonlinear polarization by the factor

$$\frac{\epsilon_{xx} + 1}{2} = \frac{\epsilon + 1}{\epsilon + 1 - c(\epsilon - 1)}, \tag{18}$$

in distinction from the three-dimension case when this factor is equal $(c + 2)/3$.

Secondly, the "mesoscopical" field acting on each column will be enhanced by the same factor in comparisoii with the macroscopic field (the permittivity ϵ_{xx} must be taken, naturally, at the considered frequencies). But these considerations do not relate to the z-component of the field since it is the same for the mesoscopic and niacroscopic fields. Thus, due to elongated mesostructure of the PS, a strong anisotropy of the nonlinear susceptibility tensor appears even for the media with the isotropic microstructures.

Finally, all these considerations may be generalized for the case of nonlinear quadrupolar medium. For this,

into the eqs. (1) we must add tlie field of a "two-dimensional" quadrupole:

$$\vec{E} = 2\pi i \frac{k}{R} \left(\frac{2}{R} H_1^{(1)} - k H_0^{(1)} \right)$$
$$[2\vec{n}(\vec{n} \cdot \vec{n} \cdot \vec{q}) - \vec{n} \cdot \vec{q}] +$$
$$+ \pi i k^3 H_1^{(1)} [\vec{n} \cdot \vec{q} - \vec{n}(\vec{n} \cdot \vec{n} \cdot \vec{q}], \qquad (19)$$

and into eq. (3) add the term $\mathbf{V} \times \mathbf{V} \times \mathbf{V}.Q$ (here $\hat{q}$ and $\hat{Q}$ are tlie planar and bulk densities of the quadrupole moment).

After rather cumbersome calculations, we come to the conclusion that the local field enhancement factor for tlic quadrupole moment is exactly tlic same as for tlie dipole one. It strongly differs from the three-dimensional case.

Therefore the enhancement relative to the bulk material of the macroscopic nonlinear susceptibily in tlie PS-type mesostructure doesn't depend on the nature of tlie nonlinearity - anharmonic, dipole, quadrupole, etc.

As a result we may be sure that, for example, for PS tlie third order nonlinear susceptibilty turns to be anisotropic value and the susceptibilty tensor components ratio for 50% porosity will be equal to 40!

VI. Summary

Tlie results obtained are essential for understanding not only tlie porous silicon optical properties, but its internal structure as well. First of all it relates to the porosity, i.e., the void fraction in crystalline silicon. Tlie effective dielectric permittivity is closely connected with tlie concentration c (formulae (8), (15), (18)). But for tlic most interesting region of high porosity (small c) this dependence is not so vivid, and so the distinction of tlie effective, dielectric permittivity ϵ_{eff} from unity will be universal for any dielectric constant c of the bulk material: $\epsilon_{eff} - 1 \sim c$. Therefore, foi a highly porous sample, an experimental accuracy of determination of ϵ_{eff} may prove to be insufficient for correct determination of the porosity. In such a situation, a proper method of tlie optical anisotropy determination may be very useful. As it follows from eq. (11), the dependence of an anisotropy 3 on c, for the material with large bulk dielectric permittivity ϵ for Si ($c \simeq 15$), takes the form $3 \sim c\epsilon$. In other words, the derivative $\frac{dB}{dc} \sim c \gg 1$. This fact may give tlie "anisotropy measurement" technique an important advantage for exact determination of the porosity by tlie optical niethods. Tlie consideration of the nonlinear susceptibility of composite materials in the three-dimensional case is given in Ref. 6.

The appearance of tlie nonlinear susceptibility anisotropy iii a highly porous sample with elongated oriented inclusions of the bulk material gives additional opportunities for their practical applications.

Acknowledgements

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