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Optical linear and third-order nonlinear properties of nano-porous Si

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In this paper, we present a systematic experimental study of effective optical linear refractive index and third-order optical nonlinear effective susceptibility of nano-porous silicon samples with various values of silicon volume fill fractions. The experimental results are in good agreement with the theoretical predictions of our simplified Bruggeman formalism for effective optical linear and third-order nonlinear susceptibilities, which was previously presented. We derived the effective linear refractive index from measurements of the nano-porous silicon reflectivity. For the third-order optical nonlinearities measurements, we used the reflection intensity scan method. A new relation for the dependence of third-order effective nonlinear optical susceptibility on the silicon volume fill fraction (for nano-porous silicon samples with silicon volume fill fraction ≤ 0.5) and on measured nonlinear reflections (at λ = 633 nm) is derived and used to get the effective third-order nonlinear susceptibility.

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1. Introduction

Nano-porous silicon is a nano-composite material with many applications in photonics, due to its convenient production processing, emission, nonlinear optical properties and infiltration possibilities. This material shows controllable linear and nonlinear optical properties, which are interesting for photonic devices (ex. optical switching, solar cells, sensors etc.) [1,2].

In a previous paper, we presented our studies of some structural and photoluminescence properties of nano-porous silicon (np-Si) [3]. Using electronic and atomic force microscopes, we have obtained information about structure of the np-Si sample surface and sizes of nano-structures and, from these data, we derived the values of Si volume fill fractions, f_{Si}, of our np-Si samples. Photoluminescence measurements allowed us to estimate the value of np-Si bandgap energy, i.e. $E_g \sim 2$ eV. In the same paper, we have presented a simplified theoretical model that helps us to calculate the effective optical linear refractive index and third-order effective nonlinear optical susceptibility of nano-porous silicon (np-Si) [3]. We assumed that nano-porous silicon has Bruggeman's geometry [1,6,7], because it is formed by two randomly intermixed components (silicon and air) and the sizes of Si structures are much smaller than the excitation light wavelength. Starting from Bruggeman model, which can describe the optical effective linear and third-order nonlinear properties of composites [1,6-8], we have derived, for np-Si, two simple semi-analytical formulae for the dependences of effective linear refractive index (n_{eff}) and for the third-order effective nonlinear susceptibility ($\chi^{(3)}_{eff}$) on Si volume fill fraction [3]. Using our simplified formalism, we can calculate, rapidly and accurately, the optical linear and third-order nonlinear parameters of a nano-porous layer necessary in realisation of a photonic device.

In this paper, we present a systematic experimental study of optical linear and third-order nonlinear properties of several np-Si samples with various values of volume fill fraction. The investigated np-Si samples were prepared by electrochemical etching and were aged for more than one year (at ambient temperature and clean environment).

In our experimental studies, we are investigating optical linear and third-order nonlinear properties of np-Si using a laser excitation with photon energy close to the estimated band-gap energy of np-Si ($E_g \sim 2$ eV), at $\lambda = 633$ nm ($h\nu_l \approx 1.96$ eV) [3]. In order to measure the n_{eff} of our np-Si samples, we have done reflectivity measurements. The experimental values of n_{eff} are in good agreement with those predicted by our simple semi-analytical formula [3] and Bruggeman model [6,7]. For measuring $\chi^{(3)}_{eff}$, we have used the reflection intensity scan (RI-Scan) method [3-5,9] and we obtained a new simple relation for describing the dependence of third-order effective nonlinear optical susceptibility on the measured nonlinear normalized reflections, for different f_{Si} (for np-Si samples with $f_{Si} \leq 0.5$). We are comparing our experimental results for third-order optical nonlinear susceptibility of np-Si samples with the theoretical predictions of our simple semi-analytical formula [3] and of Bruggeman's one and we are showing their good agreement.

2. Optical effective linear refractive index of nano-porous Si

Our nano-porous silicon samples, with various values of f_{Si}, were realized by electrochemical etching of bulk silicon (100) in hydrofluoric acid (HF). The porosity and the thickness of the nano-porous Si layers were controlled by varying the current density, the duration of etching and the HF concentration [1,2,13]. The samples were aged more than one year.

We obtained the optical effective linear refractive index of the np-Si samples by measuring their reflectivity. In the reflectivity experimental setup, we used a He-Ne laser beam (λ = 633 nm) at near normal incidence. We measured the reflectivity of three np-Si samples with various f_{Si}. The experimental data were collected in at least 20 different positions on every np-Si sample and were averaged in order to obtain a good estimation of the intensity reflectivity of our np-Si samples. We obtained the experimental values of n_{eff} using a Fresnel-type relation between reflectivity and effective linear refractive index.

We compared our experimental results with the theoretical predictions of our simplified Bruggeman formalism and of Bruggeman formula for the effective linear refractive index.

The effective linear refractive index of np-Si samples is described in the Bruggeman model [1,6,7] by following formula:

$$n_{eff}=\sqrt{\varepsilon_{eff}}=\sqrt{\frac{1}{4}\left[2-3f_{Si}+\varepsilon_{Si}(3f_{Si}-1)+\sqrt{8\varepsilon_{Si}+2-3f_{Si}+\varepsilon_{Si}(3f_{Si}-1)}\right]} \quad (1)$$

where: ε_{eff} is effective linear dielectric constant of np-Si layer and ε_{Si} is the dielectric constants of Si. Accurate results are obtained for $f_{Si} \leq 0.5$.

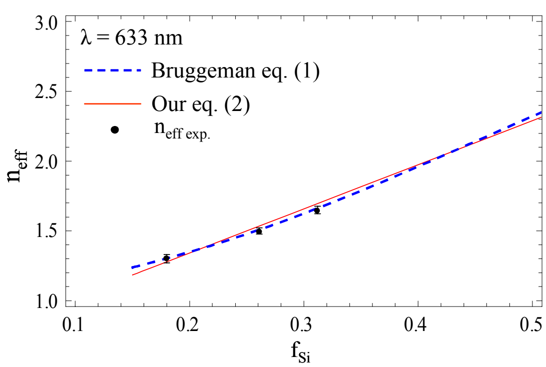

Fig. 1. Dependence of effective optical refractive index vs. Si volume fill fraction, f_{Si}: averaged experimental values of linear refractive index – black points, theoretical predictions of Bruggeman formula (1) – dashed line, theoretical predictions of our simple semi-analytical formula (2) – continuous line.

Starting from equation (1), we have obtained a simple linear semi-analytical formula for describing the effective linear refractive index of np-Si, at λ = 633 nm [3-5]:

$$n_{eff} \approx 3.16 \cdot f_{Si} + 0.71, \quad for \quad \lambda = 633\,nm, \varepsilon_{Si} = 15. \quad (2)$$

In our calculations, we used the Si dielectric constant ε_{Si} ~ 15, which was obtained by reflectivity measurements of unprocessed Si wafers.

In Fig. 1, we show the dependence of averaged experimental linear refractive index for our np-Si samples versus f_{Si}.

Also, in this figure, we represent the theoretical values provided by Bruggeman's formula (1) and by our simple semi-analytical formula (2).

In Table 1, we present the values of effective linear refractive index obtained experimentally by reflectivity measurements and the values predicted by Bruggeman formula (1) and by our simplified formula (2), for np-Si samples with various f_{Si}.

Table 1. Effective linear refractive index obtained experimentally and predicted by Bruggeman's formula (1) and by our simple semi-analytical formula (2).

f_{Si}	n_{eff}		
	Experimental data	Bruggeman eq. (1)	Our eq. (2)
0.18	1.291 ± 0.029	~ 1.303	~ 1.28
0.26	1.504 ± 0.022	~ 1.506	~ 1.53
0.308	1.650 ± 0.027	~ 1.650	~ 1.68

From Fig. 1 and Table 1, we can observe that the experimental results are certifying the theoretical predictions of our simplified Bruggeman formalism.

3. Reflection I-Scan method for experimental investigation of third-order nonlinearity of nano-porous Si

The intensity scan method (I-Scan) is a simple single beam method for determining the sign and magnitude of third-order optical nonlinear susceptibility, $\chi_{eff}^{(3)}$, in inhomogeneous thin film, with a low damage threshold [9]. Our np-Si layers have inhomogeneous structures and because they are not separated from Si wafers, we measured $\chi_{eff}^{(3)}$ of our np-Si samples by reflection I-Scan method (RI-Scan) [3, 9]. The RI-Scan experimental setup is almost the same with the setup used for reflection Z-Scan method [10-12], but in the RI-Scan case, the sample is fixed at approximately a Rayleigh length behind the focal plane of the focusing lens and the laser intensity is varied. Therefore, the RI-Scan experimental setup is simpler, without moving elements, so the misalignment or other errors introduced by optical components are reduced considerably. The reflected signal is measured by a measurement chain consisting of photo-detector, oscilloscope and PC. Thus, the advantages of RI-Scan, in comparison with RZ-Scan method, are: 1) in the RI-scan experiments, the same area of the sample is illuminated during the measurements [3,9]; 2) the sample is never passing through the focal plane, where it is exposed to a large irradiance (like in the case of RZ-Scan method) [3,9]; 3) the total exposure time is reduced and the thermal effects and other sample distortions are smaller [3,9]. The RI-Scan experimental setup is presented in Fig. 2. The np-Si samples were irradiated by a focused c.w. Gaussian beam (λ = 633 nm). For varying the intensity incident on the sample, we used a variable attenuator.

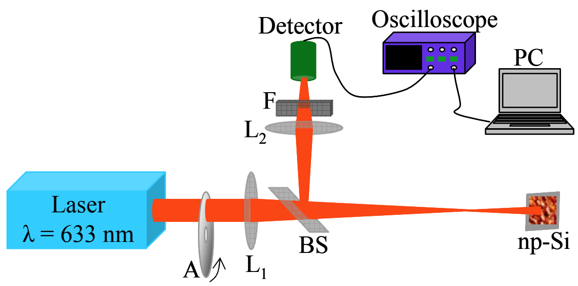

Fig. 2. RI-Scan experimental setup: c.w. laser (He-Ne or diode) (λ = 633 nm), A – variable attenuator, L_1, L_2- lenses (f_1= 12.5 cm, f_2 = 10 cm), BS – beam-splitter, F – neutral filter.

In RI-Scan method, we derived the dependence of nonlinear normalized reflection (the ratio between the power reflected by the sample with and without the nonlinear effect) on intensity as [3,10]:

$$R(I) \approx 1 + \frac{0.04}{n_{eff}^2} \cdot \frac{\chi_{eff}^{(3)} \cdot I}{\left(n_{eff}^2 - 1\right)}, \quad (3)$$

where: I is the laser beam intensity at distance z_R from the focus, $z_R = \pi w_0^2 / \lambda$ is the Rayleigh length of the beam (in this setup, z_R = 1.2 cm), $\chi_{eff}^{(3)}$ is the third-order nonlinear optical susceptibility of the sample and w_0 is the beam waist. In the case of measurements on bulk Si sample, $n_{eff} = n_{0Si}$ and $\chi_{eff}^{(3)} = \chi_{Si}^{(3)}$.

In relation (3), we replaced effective linear refractive index of np-Si, n_{eff}, with that given by our simple semi-analytical formula (2) and we obtained a new simple relation for describing the dependence of third-order effective nonlinear optical susceptibility on the measured nonlinear reflection, for different f_{Si}:

$$\frac{\chi_{eff}^{(3)}}{\chi_{Si}^{(3)}} \approx \frac{R_{np\text{-}Si} - 1}{R_{Si} - 1} \cdot \frac{1}{209} \cdot \left(3.16 \cdot f_{Si} + 0.71\right)^2 \cdot \left[\left(3.16 \cdot f_{Si} + 0.71\right)^2 - 1\right] \quad (4)$$

where: $R_{np\text{-}Si}$ and R_{Si} are normalized nonlinear reflections of the np-Si and c-Si, respectively.

We measured the third-order nonlinear optical susceptibilities of crystalline Si wafers (c-Si) (n_{0Si} = 3.87) and np-Si samples with various f_{Si}. In Fig. 3, we present our RI-Scan experimental data, which are fitted with formula (3) to get the values of third-order nonlinear optical susceptibilities of c-Si and np-Si samples, $\chi_{Si}^{(3)}$ and $\chi_{eff}^{(3)}$.

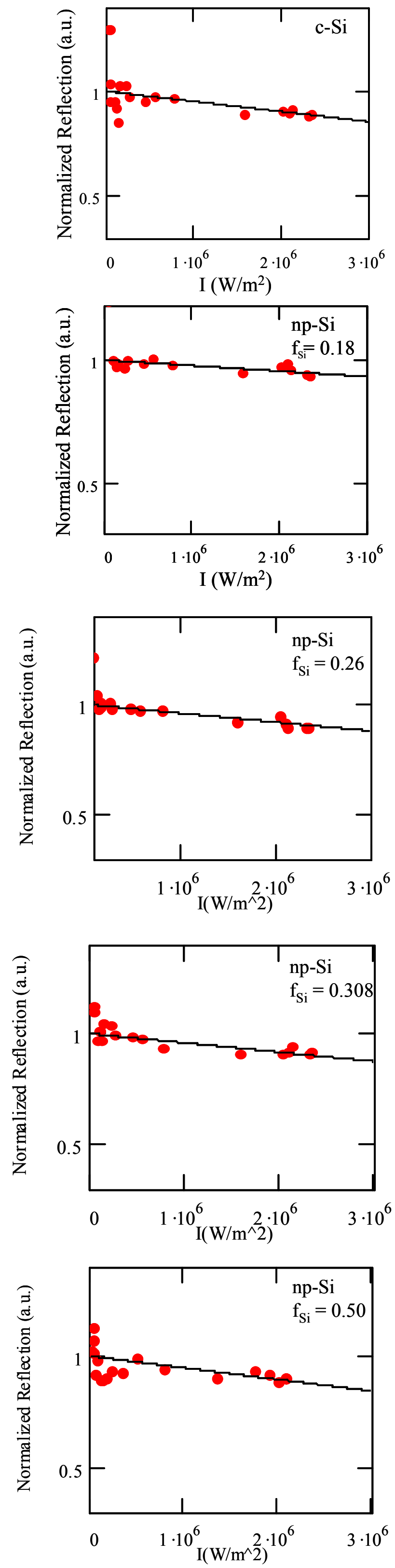

Fig. 3. Experimental data obtained with RI-Scan method for $\chi_{Si}^{(3)}$ and $\chi_{eff}^{(3)}$.

In our previous work [3-5], we have shown the Bruggeman formula [6-8] for third-order effective nonlinear optical susceptibility in the form:

$$\frac{\chi^{(3)}_{eff}}{\chi^{(3)}_{Si}} = \frac{1}{f_{Si}}\left(\frac{\partial\varepsilon_{eff}}{\partial\varepsilon_{Si}}\right)^2 = \frac{1}{f_{Si}}\left[\frac{1}{4}\left(3f_{Si}-1+\frac{2-9f_{Si}(f_{Si}-1)+\varepsilon_{Si}(1-3f_{Si})^2}{\sqrt{8\varepsilon_{Si}+(2-3f_{Si}+\varepsilon_{Si}(3f_{Si}-1))^2}}\right)\right]^2 \qquad (5)$$

We found also a semi-analytical dependence of the np-Si effective nonlinear third-order susceptibility on the Si volume fill fraction ($n_{Si} \sim 3.87$, $\lambda = 633$ nm):

$$\frac{\chi^{(3)}_{eff}}{\chi^{(3)}_{Si}} \approx 1.52 \cdot f_{Si}^2 - 0.61 \cdot f_{Si} + 0.064. \qquad (6)$$

In Fig. 4, we show the experimental data obtained with RI-Scan method, for $\chi^{(3)}_{eff} / \chi^{(3)}_{Si}$, and the theoretical predictions given by our semi-analytical formulae (4) and (6), and by nonlinear Bruggeman formula (5).

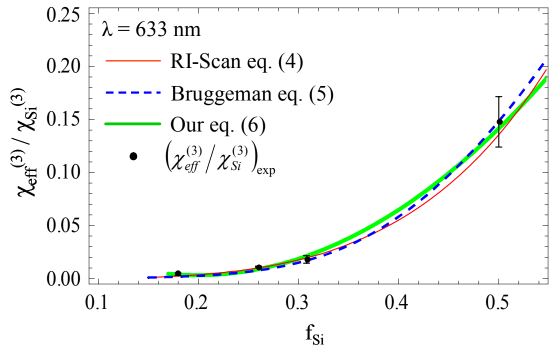

Fig. 4. Experimental results obtained with RI-Scan method for $\chi^{(3)}_{eff} / \chi^{(3)}_{Si}$ and the theoretical predictions given by our semi-analytical formulae (4) and (6), and by Bruggeman formula (5).

In Table 2, we present the values of $\chi^{(3)}_{eff} / \chi^{(3)}_{Si}$ obtained experimentally and the values predicted by our simplified formulae (4) and (6), and by Bruggeman formula (5), for our np-Si samples with various f_{Si}.

Table 2. Third-order optical nonlinear susceptibility of np-Si obtained experimentally and predicted by our semi-analytical formulae (4) and (6), and by Bruggeman formula (5).

f_{Si}	$\chi^{(3)}_{eff} / \chi^{(3)}_{Si}$			
	Experimental data	RI-Scan eq. (4)	Bruggeman eq. (5)	Our eq. (6)
0.18	$(4.075 \pm 1.154)\cdot 10^{-3}$	$2.228 \cdot 10^{-3}$	$1.78202 \cdot 10^{-3}$	$3.44800 \cdot 10^{-3}$
0.26	$(1.122 \pm 0.050)\cdot 10^{-2}$	$1.001 \cdot 10^{-2}$	$0.77693 \cdot 10^{-2}$	$0.81520 \cdot 10^{-2}$
0.308	$(1.798 \pm 0.350)\cdot 10^{-2}$	$1.952 \cdot 10^{-2}$	$1.70171 \cdot 10^{-2}$	$2.03133 \cdot 10^{-2}$
0.5	$(1.478 \pm 0.237)\cdot 10^{-1}$	$1.358 \cdot 10^{-1}$	$1.48449 \cdot 10^{-1}$	$1.39000 \cdot 10^{-1}$

One can observe that our experimental values are in a good agreement with the theoretical predictions of our simplified Bruggeman formalism (for np-Si samples with $f_{Si} \leq 0.5$).

4. Conclusions

Our experimental results for effective linear optical refractive index and for third-order effective optical nonlinear susceptibility of np-Si samples, with various f_{Si}, are verifying the theoretical predictions of Bruggeman formalism in our simplified form. We present also a new relation for the calculation of the third-order effective nonlinear optical susceptibility from the measured nonlinear reflection in RI-Scan method.

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