Determination of the effective refractive index of porous silicon/polymer composite films

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The equation for calculating the effective refractive index of porous silicon inserted polymer was obtained by three-component Bruggeman effective medium model. The dependence of the effective refractive index of porous silicon/polymer composite films on the polymer fraction with various initial porosity was given theorically and experimentally respectively. The porous silicon and polymer polymethylmetacrylate based dispersive red one (PMMA/DR1) composite films were fabricated in our experiments. It is found that the measured effective refractive index of porous silicon inserted polymer was slightly lower than the calculated result because of the oxidization of porous silicon. The effective refractive index of oxidized porous silicon inserted polymer also was analyzed by four-component medium system.

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Porous silicon, whose refractive index varies according to its porosity, is a good candidate for use in optical interconnect technology. Moreover, optical devices based on porous silicon, such as light-emitting diodes, photodetectors, and photomodulators, have already been realized. The open porous structure and the very large specific surface area of porous silicon are strong motivations for trying to introduce different kinds of materials inside the pores. The resulting composite structures can open the door to new developments mostly in the field of light emitting devices, waveguide devices, and sensors based on silicon. The porous silicon penetrated with polymer can form structures with new photoluminescence and other optical properties, or to improve the life expectancy of light emitting porous silicon, a significant improvement in the hardness and of porous silicon films with high porosity may be required[1−6]. Porous silicon, especially the high porosity porous silicon, is unstable material, and its properties and the parameters of porous silicon based devices change in storage and operation. Stabilization of porous silicon optical parameters can be helped by porous silicon penetrated with polymer. The conjugated organic polymer materials due to their large third order nonlinear optical susceptibilities and ultra response time have been applied to fabricate nonlinear optical devices. Among them, the polymer polymethylmetacrylate based dispersive red one (PMMA/DR1) is an optical materials with large optical nonlinearities and was often used to fabricate optical waveguide devices[7]. By infiltrating PMMA into the pores of porous silicon, an increase in the hardness was observed without affecting the photoluminescence intensity[6]. The porous silicon can be impregnated by DR1 dissolved in various solvent, such as butanol, propanol, and tetrahydrofurane[8]. The nonlinear absorption and nonlinear refractive index of porous silicon/DR1 composite films were enhanced obviously as compared with porous silicon at 1064 nm[9]. In this work, we have calculated the refractive index and porosity of porous layers in relation to the polymer fraction in the framework of the Bruggeman effective medium model and shown how to determine the porous silicon composition from measurements of the refractive index at a fixed wavelength.

The simplest porous silicon model is an isotropic two-component system, i.e., a silicon carcass and pores with the dimensions much less than the light wavelength λ. In this case porous silicon can be treated as an optically isotropic medium with an effective refractive index n. n is higher than that for air and lower than that for silicon and is a function of porosity. We consider layers with a low extinction coefficient when the imaginary part of the complex refractive index can be ignored, so $\mathrm{Re}\langle n\rangle \approx n$.

The two-component Bruggeman model is known to be in agreement with the experimental data for porous silicon layers on low resistivity p^+-Si substrates. The model is based on additivity of contribution from each phase into effective polarizability of the medium[10]. The Bruggeman equation for the two-component system looks like

$$f\frac{n_{\mathrm{Si}}^2-n^2}{n_{\mathrm{Si}}^2+2n^2}+p\frac{1-n^2}{1+2n^2}=0, \tag{1}$$

where n is the effective refractive index of porous silicon; p is the volume fraction of pores; $f=1-p$ is the silicon volume fraction in porous layer.

Let us assume that the initial porous silicon composition has no oxide. Porous silicon inserted polymer should be described as a three-component medium, consisting of silicon, polymer, and pores. Then the silicon volume fraction is f, the pore fraction is $p_{\mathrm{in}}=1-f$, where p_{in} is initial porosity prior of porous silicon pores filling with polymer. For the new composition of the film, Si fraction is f, polymer fraction is γ, pore fraction is $p=1-f-\gamma$. The Bruggeman equation for porous silicon inserted polymer can be written as

$$fF+\gamma G+(1-f-\gamma)V=0, \tag{2}$$

where

$$F=\frac{n_{\mathrm{Si}}^2-n^2}{n_{\mathrm{Si}}^2+2n^2},\quad G=\frac{n_{\mathrm{p}}^2-n^2}{n_{\mathrm{p}}^2+2n^2},\quad V=\frac{1-n^2}{1+2n^2},$$

n_{p} is the effective refractive index of polymer. In our assumption G and V, contrary to F, are independent of

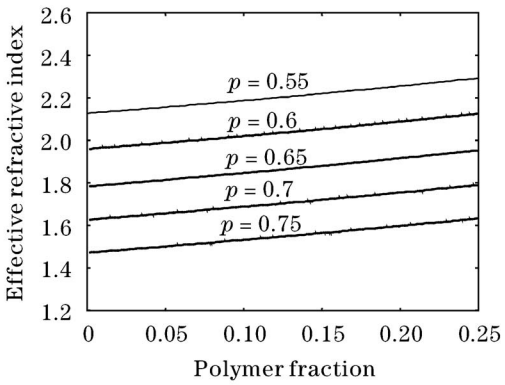

Fig. 1. Calculated dependence of the effective refractive index of porous silicon/polymer composite films on the polymer fraction with various initial porosity.

the light wavelength, as in the range that their refractive indexes are practically constant. We can obtain the polymer fraction γ

$$\gamma = \frac{fF + (1-f)V}{V - G}. \tag{3}$$

Figure 1 shows the calculated dependence of the effective refractive index of porous silicon/polymer composite on the polymer fraction for the porous silicon films with various initial porosity. Figure 1 demonstrates that polymer inserted in pores of porous silicon increases effective refractive index n.

The above formula and the graphs enable us to determine the effective refractive index from initial porosity of porous silicon and volume fraction of polymer

$$\gamma = \Delta m / CSh, \tag{4}$$

where Δm is the mass of polymer inserted in pores, C is the density of polymer, S is the area of porous silicon film, h is thickness of porous silicon film.

The single-crystal silicon wafers with p-type were used to prepare porous silicon. These Si wafers had a resistivity of 60—80 Ω·cm, a thickness of 400 μm, and a diameter of 3.5 cm. Si wafer is corroded by HF-ethanol solution in electrochemical anodization experimental setup. Ethanol can get thickness of 400 μm, and a diameter of rid of bubble on surface of Si during electrochemical etching and adjust concentration of HF solution. During the anodization process, the ratio volume of HF to ethanol is 1.5. The pulse electric current with density of 78 mA/cm^2 was used to etch the silicon wafer, pulse frequency was 10 Hz, and duty ratio is 0.2, etching time was 10 minutes. The temperature of electrolyte was 20 °C. The thickness of the porous silicon film is about 12 μm. The porosity of porous silicon was measured to be about 78% by gravimetric method.

The polymer DR1 was mixed with powder of PMMA, and the composite was dissolved into toluene. The solution was filtrated to remove foreign substance. To avoid the porous silicon sample oxidizing in air, the masses of porous silicon samples were measured quickly to keep samples freshly, and then the composite films were fabricated. In our experiment, immersion under ultrasonic agitation method was used to insert the polymer into pores of porous silicon. The sample was dry to volatilize the toluene in pores after cleaning off PMMA/DR1 on film surface of the sample.

The porosity of porous silicon was measured by the gravimetrical method using electronic weightometer. The six porous silicon inserted polymer samples were fabricated with different concentrations of PMMA/DR1 toluene solution. The thickness and refractive index were performed on the surface of porous silicon and PMMA/DR1 composite films by ellipsometric method at 633 nm. The calculated values of polymer fraction γ is 0.12—0.27 for six samples using the Eq. (4). Figure 2 indicates the relationship between the measured refractive index of composite films and polymer fraction γ in our experiment with different initial porosities. The theory results accord with experimental results well for low porosity samples. The measured effective refractive index of porous silicon of the films was lower than theory result for high porosity samples.

High porosity films on the non-degenerative substrate can be oxidized to a large extent after a short exposure to air or right after preparation. Their effective refractive index will be lower than that predicted by the three-component system silicon, polymer, and voids (Si+P+V). Besides rapid oxidation in ambient air of highly developed surfaces in high porosity porous silicon, the oxidizing process can even take place when the sample is still in the electrolyte. Hence, information about the initial porosity in these cases is unknown. However, knowing the experimental values of γ, p, and n, we can check whether they fit the three-component model, i.e., whether or not it is oxidized.

The oxidation of the internal pore surface is postulated to takes place throughout the entire film thickness and results in the formation of silicon dioxide with the refractive index $n_{SiO_2} = 1.46$. Bonding of silicon with oxygen produces a 2.27-time volume rise of the solid carcass[11]. Since the densities of Si and SiO_2 have nearly the same value (2.3 and 2.2 g/cm^3), the gravimetrically measured porosity does not practically depend on the solid carcass content and gives more or less accurate porosity value. For porous silicon that polymer has been not inserted in pores, the initial porous silicon composition was assumed that has no oxide. Assuming that some part of

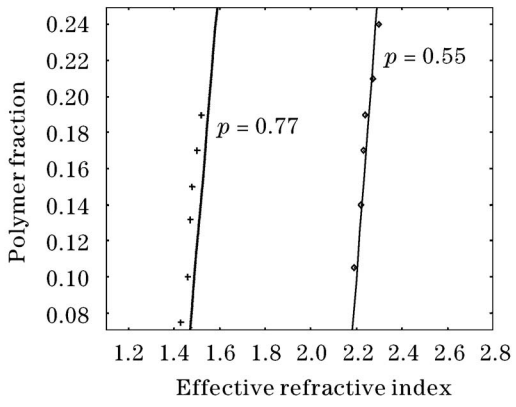

Fig. 2. The measured polymer fraction γ versus the refractive index of composite films with different initial porosity. The solid curves show the theoretical results.

the Si carcass x has been oxidized and transformed into SiO_2, occupying volume $2.27x$, the pore fraction of new composition of the film is $p = 1 - f - 1.27x$. For oxidized porous silicon inserted polymer should be described as a four-component medium, consisting of silicon, oxide, polymer, and pores. The Bruggeman equation can be written as

$$(f - x)F + 2.27xH + \gamma G + (1 - f - 1.27x - \gamma)V = 0, \tag{5}$$

where

$$H = \frac{n_{SiO_2}^2 - n^2}{n_{SiO_2}^2 + 2n^2}. \tag{6}$$

The polymer fraction γ can be expressed as

$$\gamma = \frac{fF + (1 - f)V + (2.27H - F - 1.27V)x}{V - G}. \tag{7}$$

For definite polymer fraction, the effective refractive index n of porous silicon inserted polymer decreases with the oxidation degree according to Eq. (6).

In conclusion, the dependence of polymer fraction on effective refractive index of porous silicon films with various initial porosities was studied by three-component Bruggeman model and experiment respectively. As oxidization of porous silicon, it is found that measured effective refractive index of porous silicon inserted polymer was slightly lower than calculated result. The oxidation of the internal pore surface was postulated to takes place throughout the entire film thickness and results in the formation of silicon dioxide. The effective refractive index of oxidized porous silicon inserted polymer can be analyzed by four-component medium system. For definite polymer fraction, the effective refractive index n of porous silicon inserted polymer decreases with the oxidation degree.

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