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Effect of Polymer Fraction on Refractive Index of Nanocrystalline Porous Silicon

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Abstract: Polymethyl methacrylate (PMMA) and polyvinyl pyrrolidone (PVP) are deposited on Porous Silicon (PS) substrates by spin coating technique, to make PMMA/PS and PVP/PS junctions. The porosity of the PS samples was determined using the parameters obtained from SEM images by geometrical method. SEM images indicate that the pores are surrounded by a thick columnar network of silicon walls. This porous silicon layer can be considered as sponge like structure. The refractive index of the PS samples as a function of porosity was determined by Effective Medium Approximation (EMA) methods. The influence of polymer fraction on porosity and refractive index of PS, were discussed. These results suggest that this nanocrystalline porous silicon could be a potential candidate for optical as well as optoelectronic device applications.

Key words: Porous silicon, polymethyl methacrylate, polyvinyl pyrrolidone, spin coating, refractive index

INTRODUCTION

Electrochemical dissolution of crystalline silicon in Hydrofluoric (HF) acid based electrolyte makes it as the well known as Porous Silicon (PS). The significance of the research devoted to PS has been mainly due to the efficient visible room temperature luminescence of the material (Canham, 1990; Halimaoui *et al*., 1991; Zangooie *et al*., 1999). The open porous structures, particularly the large specific surface area of PS, brought strong inducement for trying to infuse various kinds of materials inside the pores. The PS impregnated with polymer can form structures with improved photoluminescence and other optical properties (Nauyen *et al*., 2003; Li *et al*., 2000; Herino, 2000; Faiver *et al*., 1997; Kolasinski *et al*., 2000; Duttagupa *et al*., 1997). As high porosity PS is an unstable material, polymer impregnation may improve its stability. Among the various polymers Polymethyl methacrylate based dispersive red one (PMMA/DR1) and Polyvinyl pyrrolidone (PVP) are often used to fabricate optical waveguide devices (Jia, 2005; Feng *et al*., 1995) by infiltrating PMMA into the pores of PS, an increase in the hardness was observed without affecting the photoluminescence intensity (Duttagupa *et al*., 1997). Thus we have represented the refractive index and porosity of porous layers in relation to the polymer fraction employing Bruggeman effective medium model and it is shown how to determine the PS composition from measurements of the refractive index.

MATERIALS AND METHODS

The Porous Silicon (PS) samples were prepared by electrochemical anodization of p-type silicon wafers of <100> orientation, 0.5-3.0 ohm cm resistivity and of 250±0.5 μm thickness. The anodization was carried out in a mixture of HF and ethanol (volume ratio 1:2) with constant current density of 60 mA cm^{-2} and etching time of 30 min. Before the etching of silicon wafers, the samples were kept in the etching solution for 1 minute to remove the native oxide. The counter electrode was a platinum wire positioned at about 2 cm from the silicon wafer. Polymer solutions (PMMA and PVP) were prepared at different concentrations (0.5, 0.75 and 1.0%). Then PMMA and PVP solutions of different concentrations have been deposited onto PS substrates using spin coating technique. The SEM micrographs of all the samples have been obtained using a Hitachi (Model S-3000N) Scanning electron microscope employing an electron beam of accelerating voltage 20 kV.

RESULTS AND DISCUSSION

Surface morphological studies: The morphology and the size of the pores of the PS layer are related to the type of

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dopant, the orientation of the silicon substrate, the HF concentration, the current density and the illumination conditions (Prokes, 1997; Cullis *et al*., 1997). The porosity plays vital role in the fabrication of PS based devices.

The porosity of PS is defined as the quantity of silicon removed during anodization compared with the silicon concentration before anodization, evaluated in the same volume. The porosity can also be defined as a function of geometrical parameters which is written as (Salcedo *et al*., 1997; Natarajan *et al*., 2005; Natarajan *et al*., 2008; Kulathuraan *et al*., 2011).

$$P = \left(\frac{\pi}{2} * 1.732\right)\left(\frac{1}{1+\frac{m}{d}}\right)^2 \quad (1)$$

where, d indicates the average pore size and m indicates the distance between pores. Using the above said equation, we have estimated the porosity of PS and polymer (PMMA and PVP) impregnated PS.

Scanning electron micrograph of PS shows (Fig. 1) well-defined pores created due to anodic etching with very distinct boundaries. PS could be viewed as a quantum sponge and as a sponge it can be permeated by a variety of chemicals and its enormous internal surface rules its properties. Using the Eq. 1, the porosity has been estimated as 67% for PS.

When polymers are coated on the PS surface, the pores were covered with a very thin layer of PMMA and PVP polymers. From the SEM images (Fig. 2a-c and Fig. 3a-c), the porosity have been estimated for PMMA and PVP polymers impregnated PS which are given in Table 1. Increasing the concentration of polymer deposited on the PS layer, the pores were covered with thick layer of polymer and correspondingly the porosity was decreased as seen in Table 1. In comparing the coating of two polymers PMMA and PVP, the PVP polymer is more impregnated than PMMA. The reason for more impregnation of PVP may be due to its higher

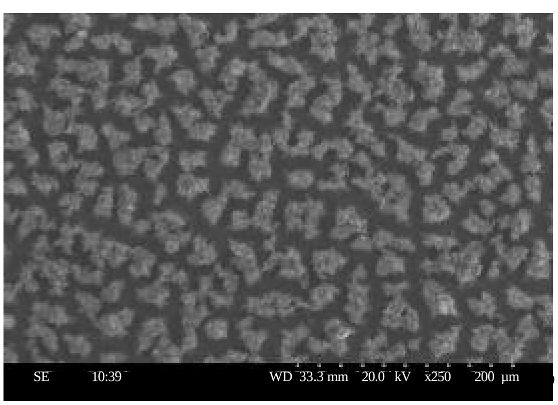

Fig. 1: SEM image of porous silicon

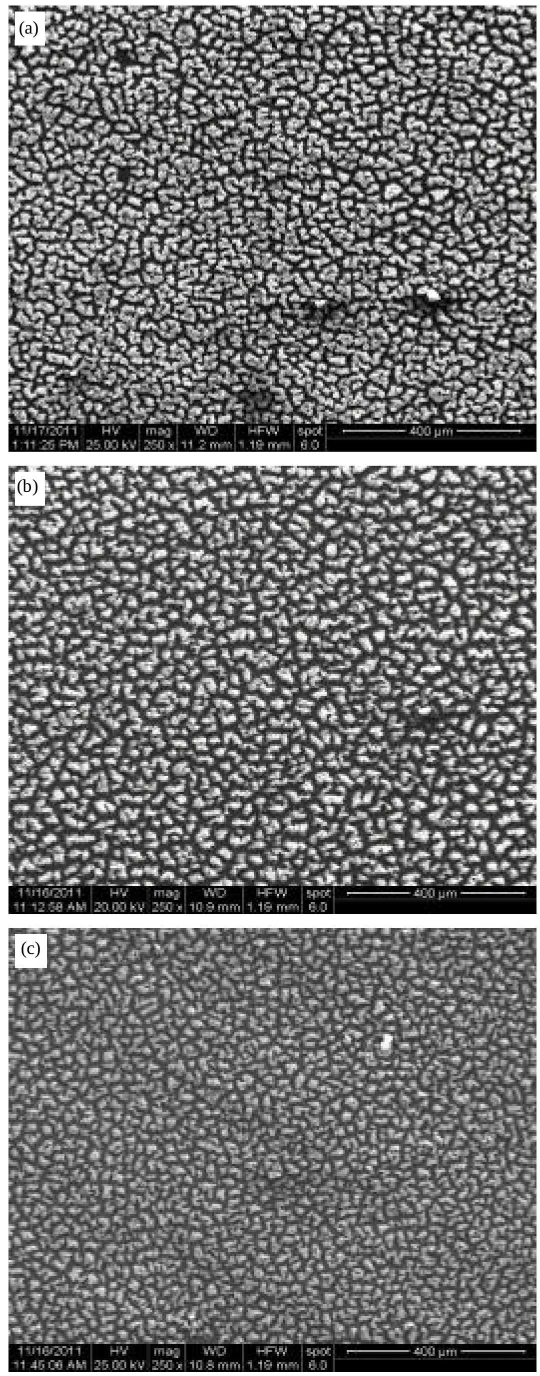

Fig. 2(a-c): SEM image of, (a) PMMA/PS (0.5%), (b) PMMA/PS (0.75%) and (c) PMMA/PS (1.0%)

Table 1: Calculated values of porosity, refractive index (n) and polymer fraction using Bruggeman effective medium approximation methods for PMMA/PS and PVP/PS at different concentrations

Samples name	Polymer concentrations (%)	Porosity (%)	Refractive index	Polymer fraction
PS[a]	---	67	1.63	---
PMMA/PS[b]	0.5	55	1.98	0.47
	0.75	44	2.40	0.89
	1.0	32	2.66	1.35
PVP/PS[c]	0.5	49	2.16	0.70
	0.75	36	2.63	1.20
	1.0	23	2.90	1.61

[a]Porous silicon, [b]Polymethyl methacrylate/porous silicon, [c]Polyvinyl pyrrolidone/porous silicon

viscosity. The SEM studies have indicated that in the case of as-formed porous silicon, uniform pore walls have been formed; however, in the case of polymer impregnated PS, the pore walls were diffused and spreading into the pore region.

Effective medium model: The PS model is an isotropic two-component system, i.e., a silicon carcass and pores with the dimensions much less than the light wavelength λ. Consequently PS can be treated as an optically isotropic medium with an effective refractive index n. Its n, which is a function of porosity, is higher than that of air and lower than that of silicon. We consider layers with a low extinction coefficient when the imaginary part of the complex refractive index can be neglected (Jia, 2005; Astrova and Tolmachev, 2000). The two-component Bruggeman model is known to be in agreement with the experimental data for PS layers on low resistivity p^+-Si substrates (Pickering *et al*., 1984). This kind of model is based on additivity of contribution from each phase into effective polarizability of the medium (Aspnes and Thecten, 1979). The Bruggeman equation for the two-component system is:

$$f\left(\frac{(n_{si})^2 - n^2}{(n_{si})^2 + 2n^2}\right) + P\left(\frac{1-n^2}{1+2n^2}\right) \qquad (2)$$

where, n is the effective refractive index of PS, P is the volume fraction of pores; f = 1-P is the silicon volume fraction in porous layers.

Let us imagine that the PS composition has no oxide. Also PS impregnated polymer can be described as a three-component medium, consisting of silicon, polymer and pores. Here f points out that the silicon volume fraction and P_{in} = 1-f, points out that the pore fraction. P_{in} is porosity prior of PS pores filling with polymers, For new composition of the film, Si fraction is f, polymers fraction is γ, pore fraction is P = 1-f-γ. The Bruggeman equation for PS impregnated polymer can be written as (Jia, 2005; Bruggeman, 1935; Astrova *et al*., 1999).

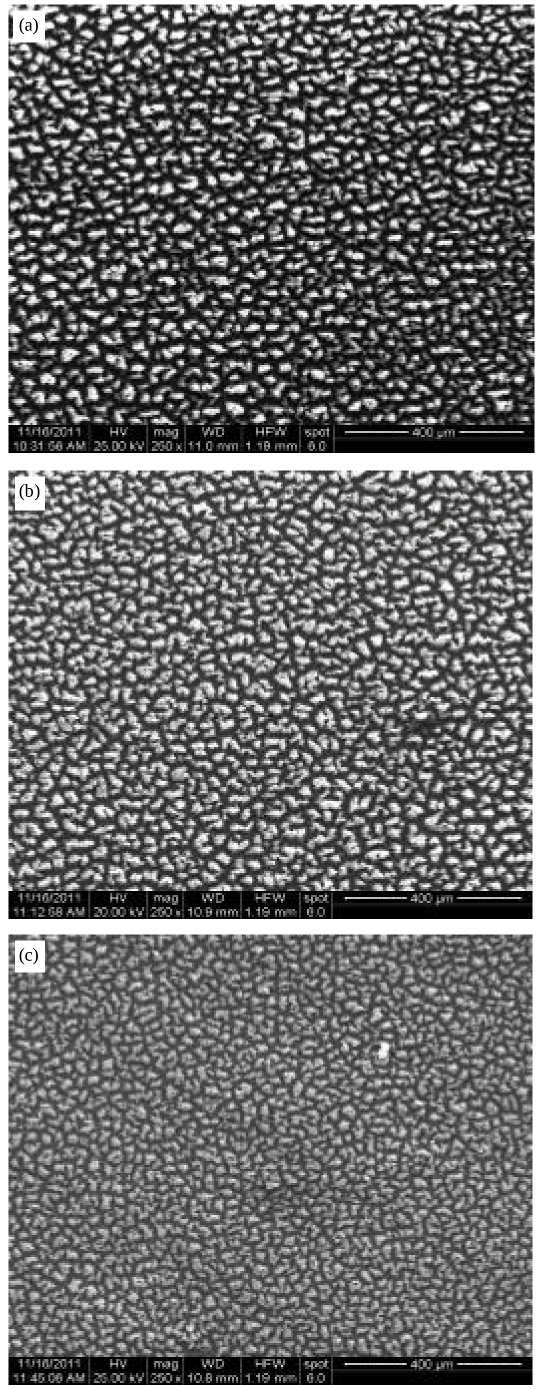

Fig. 3(a-c): SEM image of, (a) PVP/PS (0.5%), (b) PVP/PS (0.75%) and (c) PVP/PS (1.0%)

$$(fF+\gamma G + (1-f-\gamma)\, V = 0) \qquad (3)$$

Where:

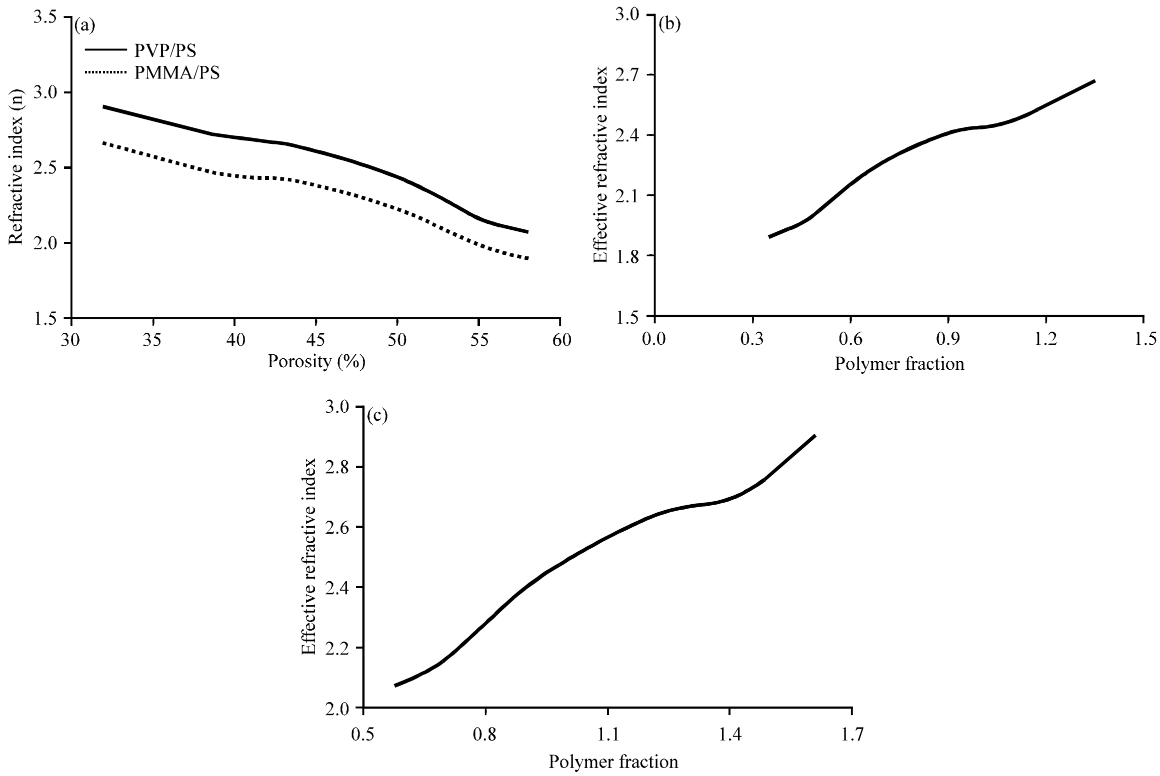

Fig. 4(a-c): Calculated values of the effective refractive index of PVP/PS and PMMA/PS composite films on the polymer fraction with various porosity for, (a) PS, (b) PMMA/PS and (c) PVP/PS

$$F = \left(\frac{(n_{si})^2 - n^2}{(n_{si})^2 + 2n^2}\right),\ G = \left(\frac{(n_p)^2 - n^2}{(n_p)^2 + 2n^2}\right) \text{ and } V = \left(\frac{1 - n^2}{1 + 2n^2}\right)$$

n_p is the effective refractive index of polymer. From the above said equation, we can obtain the polymer fraction γ:

$$\gamma = \left(\frac{fF + (1-f)V}{V - G}\right) \tag{4}$$

From the Fig. 4a, it noted that the effective refractive index of PMMA/PS and PVP/PS decreases with increase in the porosity. Figure 4b shows the calculated values of the effective refractive index of various polymer fraction of PMMA/PS and PVP/PS and also it demonstrates that polymers (PMMA and PVP)/PS composite films on the polymer fraction inserted in pores of porous silicon increases effective refractive index n. Similar results have been reported by Jia (2005) using the three-components Bruggeman approach. Jia (2005) has also pointed out that his values are lower than the experimental values for higher porosities.

CONCLUSION

SEM micrographs show uniformly distributed particles in Porous Silicon (PS). The polymers (PMMA and PVP) were deposited on PS surface by spin coating techniques. The pores are covered with very thin layer of polymers. The influence of polymers fraction on effective refractive index of PS films was studied by three-component Bruggeman model. The polymer (PMMA and PVP)/PS composite films inserted in pores of porous silicon found to increase the effective refractive index n. These results suggest that the polymer impregnated nanocrystalline porous silicon could be a potential candidate for optical as well as optoelectronic device applications.

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