Chapter 5

INFLUENCE OF POROSITY AND NITRIDATION FRACTION ON THE DIELECTRIC CONSTANT AND REFRACTIVE INDEX OF NITRATED PS: EFFECTIVE CAPACITOR MODEL

5.1 Introduction

Porous silicon (PS) is an interesting composite consisting of pores (voids) and silicon backbone networks and has a broad range of applications due to its high ratio of surface atoms that determines the high tunability of PS in many properties such as dielectric constant [1,2], band gap [3], and chemical reactivity [4,5]. However, the experimental determination of the dielectric function of PS is rather quite difficult and hence theoretical models have been developed to evaluate the dielectric function of PS. These theoretical models are based on i) the Effective Medium Approximation (EMA) and ii) addivity of contributions from each phase into the effective Polarisability of the medium. The need for the Effective Medium Approximation and its essentials are given below. As can be easily seen from the experimental data of a measurable property like thermal conductivity, the macroscopic properties depend strongly on the microstructure of the system, which is unknown in general; even if it is known to some extent, it is usually impossible to calculate how the macroscopic properties relate to the microscopic ones. Hence, some
simplifying approximations are to be made [6]. Let us restrict ourselves to
the optical properties of a system (PS) in the long wavelength limit (i.e., the
light wavelength much larger than the dimensions of inhomogeneities); this
means that we are looking for rules of “mixing” component dielectric
functions to “effective” dielectric function of the system (PS)[6]. To
achieve this, the Effective Medium Approximation (EMA) is made. The
principle of effective medium concept is shown in figures.S.1a & b for PS
consisting of two phases (components), i.e., voids (pores) embedded in
silicon matrix. This means that we have taken that particles (voids) with a
dielectric function $\varepsilon = \varepsilon_a$ are embedded in a matrix of dielectric function
$\varepsilon_M = \varepsilon_{si}$ (figures.S.1a). For light wavelengths much larger than the
characteristic size of the inhomogeneities, the microscopically
heterogeneous system (PS) fig.(S.1a) appears to be homogenous on the
macroscopic scale and hence it can be replaced by an “effective”
homogenous medium (figure 5.1b) with an “effective” dielectric function
$\varepsilon_{ef}$, [6]. So assuming (i) an effective medium for the system (PS) and (ii)
some simplified characteristics for the components (phases) of the system
(PS) and using the Polarisability relation, theoretical relations have been set
up to evaluate the effective dielectric function of the system (PS).
Traditionally the Maxwell-Garnett [7] and Bruggeman [8] methods have
been used to describe the dielectric performance of a two-phase composite
semiconductor (PS) from known dielectric functions of the constituents for
a particular topological structure [9].
The Maxwell-Garnett model considers PS as a 3d material system consisting of a mixture of Si and voids (pores) and assumes spherical particles separated by large distances. Based on this, the relation for the dielectric function of PS (called the Maxwell-Garnett equation) comes out to be

\[
(1 - P) \left[ \frac{\varepsilon_{Si} - \varepsilon_{\text{void}}}{\varepsilon_{Si} + 2\varepsilon_{\text{void}}} \right] = P \left[ \frac{\varepsilon_{PS} - \varepsilon_{\text{void}}}{\varepsilon_{PS} + 2\varepsilon_{\text{void}}} \right]
\]  

(5.1)

where P is the porosity of PS, \( \varepsilon_{Si} \), \( \varepsilon_{\text{void}} \) and \( \varepsilon_{PS} \) are the dielectric constants of silicon, void and porous silicon. This model does not give satisfactory results for PS because of the over simplifying assumptions used.[9,10]. The Bruggeman approximation, on the other hand, considers PS as a 3d isotropic mixture of C-Si and voids, and considers connected networks for porosities less than 66% and isolated particles for higher porosities. The resulting Bruggeman relation is

\[
(1 - P) \left[ \frac{\varepsilon_{Si} - \varepsilon_{PS}}{\varepsilon_{Si} + 2\varepsilon_{PS}} \right] + P \left[ \frac{\varepsilon_{\text{void}} - \varepsilon_{PS}}{\varepsilon_{\text{void}} + 2\varepsilon_{PS}} \right] = 0
\]

(5.2)
The Bruggeman approach gives fairly satisfactory results for low porous systems, but it is not satisfactory for higher porosities [9,10]. Compos.et.al.[11] simulated the effective dielectric function using a mixture of the above two models on the assumption that all the silicon inclusions are identically immersed in a homogeneous air matrix without interconnection between the crystallites.

The Looyenga approach [10] assumes a closely packed composite with interconnected networks; this leads to the Looyenga formula given by,

\[ \varepsilon_{PS}^{1/3} = (1-P)\varepsilon_{Si}^{1/3} + P\varepsilon_{void}^{1/3} \]  

The Looyenga approach is capable of giving fairly agreeable results over a wider range of porosities. [10]. A real PS structure should include air pores (voids), silicon backbone networks and surface chemical layer (SCL) (12, 13). Modeling approaches often ignore the effect of the surface/interface where chemisorptions and bond contraction occur [9]. The surface chemical layer also has a strong influence on the dielectric properties of PS. So PS should be regarded as a three component system consisting of air pores (voids), silicon and surface chemical layer (SCL) too [14]. Jugo et al. [15] have studied the dielectric properties and Astronova and Tolmachev [16] and Jia [17], the refractive index of PS in the frame work of three component system. These approaches are based on the Maxwell-Garnett and Bruggenman approximations that might be too ideal
to be suitable for the dielectric properties of PS with a three component structure [9]. However there is a simple, straight forward model called the Effective Capacitor Model (ECM), due to Pan et al. [9], which is capable of giving fairly reasonable results for the effective dielectric properties of the three component PS system. In this model (also called the Serial-parallel models [9] the porous silicon is considered to be replaced by an equivalent or effective parallel plate capacitor of capacitance $C_{\text{eff}}$ containing the effective medium with a dielectric function $\varepsilon_{\text{eff}}$.[9]. In the present work, an attempt has been made to evaluate the effective dielectric constant and hence the effective refractive index of Nitrided porous silicon structure through the Effective Capacitor Model.(ECM) and study the influence of porosity and degree of Nitridation on them.

5.2 The Effective Capacitor Model And Its Approach

5.2.1 Model for a Two-Component PS System

Since the effective dielectric constant describes the polarization response of matter (PS) to an externally applied electric field, (eg: of that of an illuminating light in an optical experiment), its dielectric properties can be derived by assuming that the PS can be replaced by an equivalent or effective parallel plate capacitor of capacitance $C_{\text{eff}}$ filled with an effective medium of dielectric constant $\varepsilon_{\text{eff}}$.[9] This effective capacitance is given by

$$C_{\text{eff}} = \frac{\varepsilon_{\text{eff}} A}{L}$$

(5.4)  

(where $A$ is the area of a plate and $L$ is the distance or separation between the two plates of the equivalent or effective capacitor respectively), from
which the effective dielectric constant $e_{\text{eff}}$ can be obtained. The effective capacitance $C_{\text{eff}}$ can be found from a combination of capacitors, obtained by replacing each component of PS by one or more parallel plate capacitors filled with the respective pure component medium as the dielectric. In this model, a cuboids structure is assumed for PS. Before proceeding further, it is pertinent to see which type of combination of component parallel plate capacitors - simple series, simple parallel or mixed (series-parallel) type- will represent the effective capacitor of PS. For simplicity, to begin with, let it be assumed that PS has only two phases/components-voids embedded in silicon matrix. The simplified parallel and series models [18,19] as illustrated in fig. 5.2a and b represent two very special geometrical structures of pore distribution and they can only predict two extreme values for the dielectric constant. These special structures do not correspond to the PS structure. An ideal two phase/component PS structure should be composed of identical air inclusions in a homogeneous silicon matrix which therefore, could only be given by a mixture of series and parallel capacitors.(i.e; mixed combination of capacitors). The cuboids cell structure for PS is given in fig. 5.2c. The top view of a cuboid cell of the two components PS based on the series-parallel model is shown in figure 5.3a. This cell consists of five parallel plate capacitors: one Q for void; two $C_2$ parallel to Q and two $C_3$ in series for silicon. The capacitor network for the two-component PS is given in figure 5.3b
a. Series Model

b. Parallel Model

Figure 5.2. Series and parallel models for two component PS

Figure 5.2c. Series – Parallel (mixed) model for two components PS

Figure 5.3a. Top view of the cuboid cell structure for two component PS.
Figure.5.3b. The capacitor network for two component PS and the effective capacitor.
The dimensions of the plates of the capacitors \( C_1, C_2, C_3 \) and \( C_{\text{eff}} \) are shown in figure 5.3c.

![Diagram showing the dimensions of the plates of the capacitors](image)

**Figure 5.3c. Dimensions of the plates of \( C_1, C_2, C_3 \) and \( C_{\text{eff}} \)**

The capacitance of a parallel plate capacitor is given by \( C = \varepsilon A/l \), where \( \varepsilon \) is the dielectric constant of the material between the two plates, \( A \) is the area of a plate and ‘\( l \)’ is the separation between the two plates.

Taking “\( d \)” to be the porous silicon layer thickness, \( N_1 \) and \( N \) as the edges of the cross section of a pore (void) and PS respectively and \( \varepsilon_\text{a} \) and \( \varepsilon_\text{Si} \) as the dielectric constant of air and silicon respectively and using the fig. 5.3(c) (i), (ii), (iii) and (iv) and using the relation given above,
\[ C_1 = \frac{\varepsilon_0 N_1 d}{N_1} = \varepsilon_d d \]  \hspace{1cm} (5.5)

\[ C_2 = \frac{\varepsilon_{SI}}{2} \frac{(N - N_1) d}{N_1} = \frac{\varepsilon_{SI} (N - N_1) d}{2N_1} \]  \hspace{1cm} (5.6)

\[ C_3 = \frac{\varepsilon_{SI} N d}{(N - N_1)} = \frac{\varepsilon_{SI} 2Nd}{N - N_1} \]  \hspace{1cm} (5.7)

\[ C_{\text{eff}} = \frac{\varepsilon_{\text{eff}} N d}{N} = \varepsilon_{\text{eff}} d \]  \hspace{1cm} (5.8)

But from the capacitor network shown in figure (5.3b)

\[ \frac{1}{C_{\text{eff}}} = \frac{1}{C_1 + 2C_2} + \frac{2}{C_3} \]  \hspace{1cm} (5.9)

Hence

\[ C_{\text{eff}} = \frac{1}{\frac{1}{C_1 + 2C_2} + \frac{2}{C_3}} \]

Taking the equation (5.9) and using the relations (5.5) to (5.8)

\[ \frac{1}{\varepsilon_{\text{eff}} d} = \frac{1}{\varepsilon_d + 2\varepsilon_{SI} N - N_1} \frac{N_1}{N} + \frac{2}{\varepsilon_{SI} 2N N - N_1} \]

Simplifying and rearranging

\[ \varepsilon_{\text{eff}} = \frac{\varepsilon_{SI} \left( \frac{N}{N_1} \right) \varepsilon_{SI} + \left( \frac{1}{1 - \left( \frac{N_1}{N} \right) \right)} {\varepsilon_d + \left( \frac{N - N_1}{N} \right) + \varepsilon_d} \]  \hspace{1cm} (5.10)

Defining the Porosity of the sample to be,

\[ P = \frac{\text{Volume of pore(void)}}{\text{Volume of PS}} = \frac{V_{\text{void}}}{V_{PS}} \]

\[ = \frac{N_1 \times N_1 \times d}{N \times N \times d} = \frac{N_1^2}{N^2} \]  \hspace{1cm} (5.11)
Using this in the equation (5.10) and simplifying, the effective dielectric constant of two component PS (i.e., of the as etched PS) becomes
\[
\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{Si}} [(1 - \sqrt{P}) \varepsilon_{\text{Si}} + (\sqrt{P}) \varepsilon_{a}]}{(1 - \sqrt{P} - P) \varepsilon_{\text{Si}} + (\sqrt{P} - P) \varepsilon_{a}}
\]  
(5.12)

5.2.2. Model for three-component PS system

Changing the composition of the electrolyte used for the anodization process as well as post formation treatments would result in the formation of a chemical layer on the surface of PS. This surface chemical layer (SCL) will also have a strong influence on the dielectric properties of PS. Taking that this chemical layer is formed around the pores, the system will have three components - void (pore), surface chemical layer (SCL) and silicon backbone networks, the surface chemical layer surrounding the pore and the silicon surrounding the surface chemical layer.
The top view of the cell structure for the three component PS system is shown in the figure (5.4a).

**Figure 5.4a: Top view of the series-parallel cell structure of the three component PS system**

From the figure.5.4a, it is seen that the cell contains nine parallel plate capacitors: one $C_1$ for void, two $C_4$ in parallel to $C_1$ and two $C_5$ in series to them for the surface chemical layer, two $C_2$ parallel to the over all system for silicon and two $C_3$ in series to the over all system for silicon.
The capacitor network for this system is shown in figure 5.4b,

\[
\frac{1}{C'} = \frac{1}{C_1 + 2C_4} + \frac{2}{C_5}
\]

\[
\frac{1}{C''} = \frac{1}{2C_2}
\]

\[
\frac{1}{C''' = \frac{2}{C_3}}
\]

Figure 5.4b The capacitor network for three component PS and the effective capacitor.

\[
\frac{1}{C_{eff}} = \frac{1}{(1/(1/(1\times(2C_4 + C_1) + (2/C_5)) + 2C_2) + 2/C_3)}
\]

(5.13)
The dimensions of the plates of the capacitors \( C_1, C_2, C_3, C_4, C_5 \) and \( C_{\text{eff}} \) are shown in figure 5.4c.

**Figure 5.4c:** Dimensions of plates of \( C_1, C_2, C_3, C_4, C_5 \) and \( C_{\text{eff}} \)

Using the figure 5.4c and taking \( \varepsilon_{\text{SCL}} \) as the dielectric constant of the surface chemical layer (SCL)

\[
C_i = \frac{\varepsilon_a N_1 d}{N_1} = \varepsilon_a d
\]  

(5.14)
\[ C_2 = \varepsilon_{si} \frac{(N - N_t - 2N_2)d}{2(N_t + 2N_2)} \]  
(5.15)

\[ C_3 = \varepsilon_{si} \frac{2Nd}{N - N_t - 2N_2} \]  
(5.16)

\[ C_4 = \varepsilon_{scl} \frac{N_2 d}{N_t} \]  
(5.17)

\[ C_5 = \varepsilon_{scl} \frac{(N_t + 2N_2)d}{N_2} \]  
(5.18)

Substituting \( C_1, C_2, C_3, C_4 \) and \( C_5 \) from equations (5.14 to 5.18) in equation (5.13),

\[ \frac{1}{\varepsilon_{eff}d} = \left[ \frac{1}{1} \right] \left[ \frac{1}{1} \right] \left[ \frac{1}{(2\varepsilon_{scl} \frac{N_2 d}{N_t} + \varepsilon_{t}d) + \frac{2N_2}{\varepsilon_{scl} (N_t + 2N_2)d} + 2\varepsilon_{cl} \frac{(N - N_t - 2N_2)d}{2(N_t + 2N_2)} + \frac{2(N - N_t - 2N_2)}{\varepsilon_{si} 2Nd}} \right] \]  
(5.19)

Let us take (i) the porosity \( P \) from equation (5.11), (ii) the thickness ratio \( x = \frac{N_2}{N_t} \) of the surface chemical layer to the void and (iii) the chemical fraction \( F \), as the volume ratio of, \( V_{scl} \), to the sum of \( V_{si} \) and \( V_{scl} \).

\[ F = \frac{V_{scl}}{V_{si} + V_{scl}} = \frac{4N_t N_2 + 4N_2^2}{N^2 - N_t^2} = \frac{4P x + x^2}{1 - P} \]  
(5.20)

Expressing \( x \) in terms of \( F \) & \( P \)

\[ x = \left( \frac{1}{2} \sqrt{1 + \left( \frac{F}{P} \right) (1 - P) - 1} \right) \]  
(5.21)

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By definition, the chemical fraction $F$ can have values from 0 to 1. When $F=0$, the PS consists of only two components: silicon and voids; if $F$ is such that $0<F<1$, the surface is having partial chemical layer formation, now the system (PS) consists of three components: silicon, surface chemical layer (SCL) and voids, when $F=1$, the PS has complete chemical layer formation and the silicon phase disappears and a different two component system consisting of the surface chemical layer (SCL) and voids is formed.

Using equation (5.11), (5.20) and (5.21) in the equation (5.19) and taking

$$
A_1 = 2(1 + 2x)^2 x \sqrt{P} \\
A_2 = (1 + 2x)^2 x \sqrt{P} \\
A_3 = (1 - \sqrt{P} - 2x - \sqrt{P})[1 + 2x + 4x^2] \\
A_4 = \sqrt{2} (1 - \sqrt{P} - 2x - \sqrt{P})x \\
B_1 = 2(1 + 2x)^2 x - \sqrt{P} [(1 - \sqrt{P} - 2x - \sqrt{P})] \\
B_2 = (1 + 2x)^2 x \sqrt{P} (1 - \sqrt{P} - 2x - \sqrt{P}) \\
B_3 = (1 + 2x + 4x^2) [(1 + 2x) - \sqrt{P} + (1 - \sqrt{P} - 2x \sqrt{P})^2] \\
B_4 = 2x [(1 + 2x) \sqrt{P} + (1 - \sqrt{P} - 2x \sqrt{P})^2]$$

(5.22)

(where $A$’s and $B$’s are constants, which depend on the porosity) and simplifying, the effective dielectric constant of three component PS system becomes

$$
\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{Si}} [A_1 \varepsilon_{\text{SCL}} + A_2 \varepsilon_{\text{SCL}} \varepsilon_a + A_3 \varepsilon_{\text{SCL}} \varepsilon_{\text{Si}} + A_4 \varepsilon_{\text{Si}} \varepsilon_a]}{B_1 \varepsilon_{\text{SCL}}^2 + B_2 \varepsilon_{\text{SCL}} \varepsilon_a + B_3 \varepsilon_{\text{SCL}} \varepsilon_{\text{Si}} + B_4 \varepsilon_{\text{Si}} \varepsilon_a}
$$

(5.23)

The effective refractive index of the porous system $n_{\text{eff}}$ can be computed using the relation

$$
n_{\text{eff}} = (\varepsilon_{\text{eff}})^{1/2}
$$

(5.24)
Using equations 5.23 and 5.24, $e_{\text{eff}}$ and $n_{\text{eff}}$ have been evaluated for various porosities and for various chemical fractions of Nitried PS through Microsoft Excel.

5.3 Results and Discussion

The experimental studies on the effect of addition of HN0$_3$ to the HF-ethanol solution to form the electrolyte for the anodizing process, have indicated that there is the possibility of formation of Silicon Nitride ($\text{Si}_3\text{N}_4$) as the surface layer in the resulting PS. (Chapter 4B). The PS thus formed could be termed as Nitrated PS. The Nitrated PS is a three component system consisting of voids (pores), silicon (Si) and surface silicon nitride ($\text{Si}_3\text{N}_4$) layer. It could be noted that i) when F=0 the PS consists of two components - voids and silicon and is nothing but the as-etched PS, ii) when 0<F> 1. the system will have three components - voids, silicon and silicon nitride layer and Nitrified PS results, and iii) when F=1, a different two component system consisting of voids and silicon nitride ($\text{Si}_3\text{N}_4$) is formed and now the system is porous silicon nitride. Porous Silicon Nitride has potential applications in electronic circuitry [20]. It will be of interest to evaluate the effective dielectric constant and the effective refractive index of Nitried PS for various porosities (P) and various Nitrification fraction(chemical fraction)(F), using the Effective Capacitor model.
Taking the dielectric constants of silicon, void and silicon nitride $\text{Si}_3\text{N}_4$ as $\varepsilon_a=13.1$, $\varepsilon_v=1$ and $\varepsilon_{\text{SCL}} = 7.5$ (SCL= $\text{Si}_3\text{N}_4$ in the present case), and varying the porosity from 40% to 90% in steps of 10% and the nitridation fraction (chemical fraction) from 0 to 1 in steps of 0.2, the data
have been processed using Microsoft Excel and the effective dielectric constant $e_{\text{eff}}$ and the effective refractive index $n_{\text{eff}}$ of nitrided PS have been evaluated for the chosen porosities (P) and chosen Nitridation fraction (F). The results obtained are shown in fig 5.5 and 5.6. From the figures, it can be seen that the effective dielectric constant and the effective refractive index of Nitrided PS decrease with i) porosity (P) and ii) Nitridation degree (F). When the porosity (P) increases, the void fraction in the PS increases and hence there could be a decrease in the effective dielectric constant and the effective refractive index of PS. Similarly when the Nitridation fraction F increases, $\text{Si}_3\text{N}_4$ fraction in PS increases and because of this, there could be a decrease in the effective dielectric constant and effective refractive index of PS. Similar trends have been reported by Pan et.al, [9] and Natarajan et al [21] from their studies on oxidized PS and chlorinated PS. The extrapolation of the curves in figures 5.5 & 5.6 to the higher porosity side indicates that all the dielectric constant curves converge to $e_{\text{eff}}$=1 and all the refractive index curves to $n_{\text{eff}}$=1 at 100% porosity. Also the available experimental data [9,17] for F=0 (i.e for as-etched PS) plotted in the same figures (shown as □ in the figures) lie close to the curves for F=0 obtained from the present study. A value of 2.2 for the effective dielectric constant of Porous Silicon Nitride (F=i case) with 60% porosity obtained from the present study is close to the experimental value of 2.4 reported by Jie-Xu et al.(22) for Porous Silicon Nitride ceramics with a similar porosity. All these validate the methodology used in the present study.
5.4. Conclusion

The study has demonstrated that the simple Effective Capacitor Model is capable of giving reasonable effective dielectric constant and effective refractive index values for the Nitrided porous silicon over different porosities and different Nitridation degrees.

5.5 References