

## RAYLEIGH SCATTERING FROM SINGLE-SITE POLYSYLANE ADSORBED ON SILICON: THEORY

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An ordered set of dipoles with mutual interaction in the close vicinity of a dielectric surface is studied. The solution of that particular theoretical problem is given rigorously both for the static and dynamic case. It can serve as a description of the polysilane molecules formed at the surface of silicon by means of HOMOCVD or sputtering in a hydrogen atmosphere. The theory can be used to describe the optical behaviour of those molecules, like first the Rayleigh scattering and next also the photoluminescence of those molecules.

### 1. Introduction

Spear and Le Comber [1] were probably the first to contribute to the present activities in the field of hydrogenated amorphous silicon. The fact that the amount of hydrogen stored in these type of samples exceeded the number of dangling bonds by about a factor of 100, indicated that in this process more was going on than a simple surface adsorption. Spectroscopic analysis, especially by means of IR spectroscopy and Raman techniques (see e.g. ref. [2]), started to point gradually in the direction of formation of  $(\text{SiH}_2)_n$ -type of chains at the surface of these materials. For both types of production of those novel materials – homogeneous chemical vapour deposition [3] and RF plasma sputtering [4] – existence of  $(\text{SiH}_2)_n$  chains seems to be established. Interest in hydrogenated amorphous silicon was further stimulated by the discovery of its photoluminescent properties [4-6]. Though emitted over a wider energy interval, a-Si:H exhibits a five times larger photoluminescence intensity (for HOMOCVD produced films) as compared to existing commercial LED materials [4].

The larger band gap, as compared to ordinary a-Si:H, required by such observations, asks for calculations of the electronic structure, as were done assuming vacancies [7,8] or assuming formation of polysilane chains [9]. The latter, more relevant approach, yields satisfying gap values, but the observed

intensities remain unexplained. As such very useful information might be gathered from surface Rayleigh scattering experiments.

A rigorous theoretical solution of this problem being beyond the present abilities, we will base this article upon the assumptions customary in the theory of Rayleigh scattering from surfaces and from large molecules in the gas phase. Concerning the latter the classical induced-dipole model is the prevailing method and here the obvious similarity between alkanes and polysylanes has to be emphasized. From alkanes it is known that a straightforward application of this model yields unrealistic results and one needs to screen the internal interactions with a certain factor  $\epsilon_s$  to obtain realistic results [10,1]. With respect to the influence of the surface, represented by a homogeneous halfspace characterized by a complex dielectric constant  $\bar{\epsilon}$ , we will investigate two models. Firstly, a static model will be used where the polysilane molecule interacts with the surface through image interaction. The molecule itself will be presumed to reside above the surface. Secondly, a dynamic model will be presented based on a mathematically rigorous solution for a radiating dipole above a dielectric surface, using the method of Sommerfeld.

## 2. Image field solution

More detailed information about the image field method, as applied to surface Rayleigh/Raman problems can be found in ref. [12]. First a separate polysilane will be considered briefly in the same way as in ref. [10]. The polysilane will be represented by a finite number  $N$  of discrete dipoles, positioned at  $\mathbf{r}_i$  and connected to their local field through

$$\mathbf{p}_i = \alpha_i \mathbf{E}_{\text{loc}}(\mathbf{r}_i) \tag{1}$$

$\alpha_i$  represents as usual the polarizability of the corresponding dipole.

This defines the configuration to be used, depending on whether one assigns the dipole to the atom (site model) or to the bonding (backbone model). At short distances the dipole field can be approximated by the induction field alone, hence allowing for a (quasi-) static approach. Now the explicit form of (1) becomes ( $\mathbf{E}_{\text{ext}}$  represents the incoming field)

$$\mathbf{p}_i = \alpha_i \left( \mathbf{E}_{\text{ext}} + \frac{1}{4\pi\epsilon_0} \sum_{j \neq i} \frac{1}{r_{ij}^3} \boldsymbol{\tau}_{ij} \mathbf{p}_j \right), \tag{2}$$

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|, \quad \boldsymbol{\tau}_{ij} = 3 \hat{\mathbf{r}}_{ij} \hat{\mathbf{r}}_{ij} - \mathbf{1}$$

Taking into account all dipoles, (2) transforms into a system of linear equations from which one derives, after introducing the abbreviations  $\alpha_0 = \epsilon_0 a^3$ ,  $\mathbf{C}_i = (4\pi\alpha_0) \alpha_i^{-1}$  and  $\boldsymbol{\pi}_i = \mathbf{p}_i/\alpha_0 |\mathbf{E}_{\text{ext}}|$ , the dimensionless system of interaction equations

$$\mathbf{A} \boldsymbol{\pi} = 4\pi \hat{\boldsymbol{\epsilon}} \quad (3)$$

$\boldsymbol{\pi}$  is a composite vector containing all separate  $\boldsymbol{\pi}_i$ ,  $a$  is the Bohr radius. Equivalently  $\hat{\boldsymbol{\epsilon}}$  contains  $N$  times the unit vector controlling  $\mathbf{E}_{\text{ext}}$ . The matrix  $\mathbf{A}$  has an  $(N \times N)$  dyadic structure with explicit form

$$\mathbf{A}_{ii} = \mathbf{C}_i, \quad \mathbf{A}_{ij} = -\boldsymbol{\tau}_{ij}/Q_{ij}^3 \epsilon_s \quad (i \neq j, r_{ij} = aQ_{ij}) \quad (4)$$

The screening factor  $\epsilon_s$ , being almost exactly 10 for alkanes [11], is necessary to obtain realistic results, as emphasized in ref. [10]. Placing next a surface close to the polysilane molecule causes a modification of eq. (3). For a single dipole  $\mathbf{p}$  at a height  $z$  above a dielectric surface characterized by a dielectric constant  $\bar{\epsilon}$ , a solution fulfilling the boundary conditions

$$\mathbf{E}_{\parallel}^+ = \mathbf{E}_{\parallel}^-, \quad \mathbf{E}_{\perp}^+ = \bar{\epsilon} \mathbf{E}_{\perp}^- \quad (5)$$

is obtained through adding an image dipole  $\mathbf{p}'$  at  $-z$  as in ref. [12]

$$\mathbf{p}' = \boldsymbol{\eta} \mathbf{p}, \quad \boldsymbol{\eta} = \frac{\bar{\epsilon} - 1}{\bar{\epsilon} + 1} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad (6)$$

where the  $z$ -axis is supposed to be perpendicular to the surface. Solving now for the entire polysilane molecule, we require every dipole in the chain to produce an image dipole according to (6). This procedure guarantees the obeying of the boundary conditions, throughout the procedure.

Now  $\mathbf{E}_{\text{ext}}$  is the sum of the incoming and reflected beam. So we arrive at the equivalent expression of eq. (1)

$$\mathbf{p}_i = \boldsymbol{\alpha}_i \left[ \mathbf{E}_{\text{ext}} + \frac{1}{4\pi\epsilon_0} \left( \sum_{j \neq i}^N \frac{1}{(r_{ij}^+)^3} \boldsymbol{\tau}_{ij}^+ \mathbf{p}_j + \sum_{j=1}^N \frac{1}{(r_{ij}^-)^3} \boldsymbol{\tau}_{ij}^- \boldsymbol{\eta} \mathbf{p}_j \right) \right], \quad (7)$$

$$\mathbf{r}_{ij}^+ = \mathbf{r}_i^+ - \mathbf{r}_j^+, \quad \mathbf{r}_{ij}^- = \mathbf{r}_i^+ - \mathbf{r}_j^-$$

Position vectors with upper index  $-$  have  $z$  component reversed as compared to their  $+$  counterparts. The dyadics for the interaction matrix now become

$$\mathbf{A}'_{ii} = \mathbf{C}_i - (\boldsymbol{\tau}_{ii}^- \boldsymbol{\eta})/\epsilon_s (Q_{ii}^-)^3, \quad \mathbf{A}'_{ij} = -[\boldsymbol{\tau}_{ij}^+/\epsilon_s (Q_{ij}^+)^3 + (\boldsymbol{\tau}_{ij}^- \boldsymbol{\eta})/\epsilon_s (Q_{ij}^-)^3] \quad (8)$$

$\epsilon_s$  has the equivalent meaning as in (4). Due to the influence of the surface, the diagonal elements reduce, giving rise to unstable solutions [10,11]. The remedy has to be sought in screening of the image fields by  $\epsilon_s$ , varying from 1 (physisorption) to 10 (chemisorption) or more generally as a function of  $z$ .

### 3. Dynamic solution: Sommerfeld's method

As far as the classical dynamic treatment of a single dipole above a dielectric surface is concerned, refs [13,14] build a good introduction For the dynamic solution one needs Sommerfeld's method [15] with boundary conditions

$$E_{\parallel}^+ = E_{\parallel}^-, \quad H_{\parallel}^+ = H_{\parallel}^- \tag{9}$$

Using the expansion of the spherical wave in Bessel functions the result follows in a way closely resembling (7)

$$p_i = \alpha_i \left[ E_{\text{ext}} + \frac{1}{4\pi\epsilon_0} \left( \sum_{j \neq i} \mathbf{T}_{ij}^+ p_j + \sum_{j=1}^N \int_0^{\infty} dk \frac{e^{-u_0(z-z_j)}}{u_0} \mathbf{T}_{ij}^-(k) p_j \right) \right],$$

$$u_0 = (k^2 - k_0^2)^{1/2} \tag{10}$$

Besides previous definitions, we assume here an incoming wave of frequency  $\omega$ , but in (10) the frequency-dependent exponential is divided out, leaving only (complex) amplitudes  $k_0$  represents the in vacuo wavenumber It remains to define the two dyadic tensors

The first one  $\mathbf{T}^+$  governs the direct interactions between the dipoles representing the polysylane molecule

$$\mathbf{T}_{ij}^+ = g_1(r_{ij}^+) \mathbf{1} + g_2(r_{ij}^+) \hat{r}_{ij}^+ \hat{r}_{ij}^+,$$

$$g_1(r) = \frac{e^{ik_0 r}}{r} \left( k_0^2 + \frac{ik_0}{r} - \frac{1}{r^2} \right),$$

$$g_2(r) = \frac{e^{ik_0 r}}{r} \left( -k_0^2 - \frac{3ik_0 r}{r} + \frac{3}{r^2} \right) \tag{11}$$

Interaction through reflected contributions follows from the integral in (10), where the important factor is  $\mathbf{T}^-(k)$ , given as

$$T_{ij,tt}^- = [(k^2 - k_0^2)R_e(k) - k_0^2 R_m(k)] h(t_{ij}, s_{ij}) + k k_0^2 R_m(k) J_0(k s_{ij}),$$

$$T_{ij,zz}^- = R_e(k) k^3 J_0(k s_{ij}), \tag{12}$$

$$T_{ij,yy}^- = [(k^2 - k_0^2) R_e(k) - k_0^2 R_m(k)] \left[ \frac{k x_{ij} y_{ij}}{(s_{ij})^2} J_2(k s_{ij}) \right] = -T_{ij,xx}^-,$$

$$T_{ij,tz}^- = \left[ R_e(k) \left( \frac{(k^2 - k_0^2)^{1/2} k^2 t_{ij}}{s_{ij}} \right) J_1(k s_{ij}) \right] = -T_{ij,zt}^-$$

In eqs (12)  $J_0, J_1, J_2$  represent the well-known Bessel functions of the first kind Further the following definitions were used

$$\begin{aligned}
 h(t, s) &= J_1(k, s)/s - kt^2 J_2(ks)/s^2, \quad s = (\kappa^2 + \nu^2)^{1/2}, \\
 R_e(k) &= \frac{\bar{\epsilon}(k^2 - k_0^2)^{1/2} - (k^2 - \bar{\epsilon}k_0^2)^{1/2}}{\bar{\epsilon}(k^2 - k_0^2)^{1/2} + (k^2 - \bar{\epsilon}k_0^2)^{1/2}}, \\
 R_m(k) &= \frac{(k^2 - k_0^2)^{1/2} - (k^2 - \bar{\epsilon}k_0^2)^{1/2}}{(k^2 - k_0^2)^{1/2} + (k^2 - \bar{\epsilon}k_0^2)^{1/2}} \tag{13}
 \end{aligned}$$

$t$  represents both  $x$  and  $y$ . Since  $x, y$  are unaffected under reflection the  $\pm$  upper index can be neglected in  $x, y$  and  $s$  represents again the complex relative dielectric constant of the dielectric half-space. The dyadics for the interaction matrix are defined now as

$$\begin{aligned}
 \mathbf{A}_{ij}'' &= \mathbf{C}_i - \int_0^{\infty} dk \frac{e^{-u_0(z_{ij})}}{u_0} a^3 \mathbf{T}_{ij}^-(k), \\
 \mathbf{A}_{ij}'' &= - \left( a^3 \mathbf{T}_{ij}^+ + \int_0^{\infty} dk \frac{e^{-u_0(z_{ij})}}{u_0} a^3 \mathbf{T}_{ij}^-(k) \right) \tag{14}
 \end{aligned}$$

Each of the components of (14) can be screened in exactly the same manner as in (8), which is probably the only way to obtain realistic predictions from this model. As a result after solving of the interaction equations the separate dipole values  $\mathbf{p}$  or  $\boldsymbol{\pi}$  are obtained. This is all what is required for further use later on.

**4. Remote fields: intensity pattern**

In general what is wanted in explaining Rayleigh scattering experiments, is the intensity at large distances from the illuminated spot at the surface. The remote electric fields follow in two steps. First define the total polarizability  $\boldsymbol{\alpha}_{\text{tot}}$  for the surface molecule

$$\boldsymbol{\alpha}_{\text{tot}} = 4\pi\alpha_0 \sum_{i,j=1}^N \mathbf{A}_{ij}^{-1} \tag{15}$$

Defining next the Fresnel reflection matrix  $\mathbf{R}(\theta)$  as

$$\begin{aligned}
 \mathbf{R}(\theta) &= \begin{pmatrix} 1 + R_m(\theta) & 0 & 0 \\ 0 & 1 + R_e(\theta) & 0 \\ 0 & 0 & 1 + R_m(\theta) \end{pmatrix} \tag{16} \\
 R_e(\theta) &= \frac{\bar{\epsilon} \cos \theta - (\bar{\epsilon} - \sin^2 \theta)^{1/2}}{\bar{\epsilon} \cos \theta + (\bar{\epsilon} - \sin^2 \theta)^{1/2}}, \quad R_m(\theta) = \frac{\cos \theta - (\bar{\epsilon} - \sin^2 \theta)^{1/2}}{\cos \theta + (\bar{\epsilon} - \sin^2 \theta)^{1/2}}
 \end{aligned}$$

Here, as in ref. [13], the presupposition was used that the  $x$ -axis coincides

with the projection of the incident wavevector. The angle of this wavevector with the  $x$ -axis is  $\theta_0$ . Now the total polarizability of the molecule  $\mathbf{p}_{\text{tot}}$  is connected to the incident field  $\mathbf{E}_{\text{inc}}$  through

$$\mathbf{p}_{\text{tot}} = \alpha_{\text{tot}} \mathbf{R}(\theta_0) \mathbf{E}_{\text{inc}}' \quad (17)$$

Since we suppose also that the size of the molecule is much smaller than the wavelength of the light used, the following treatment of the second step is allowed. Using the asymptotic solutions given in ref. [15], the remote field  $\mathbf{E}_{\text{rem}}$  detected at  $\mathbf{R}$ , where the corresponding unit vector makes an angle  $\theta$  with the  $z$ -axis, follows from

$$\mathbf{E}_{\text{rem}}(\mathbf{R}) = k_0^2 \frac{e^{ik_0 R}}{4\pi\epsilon_0 R} \boldsymbol{\tau}_{\text{rem}} \mathbf{R}'(\theta) \alpha_{\text{tot}} \mathbf{R}(\theta_0) \mathbf{E}_{\text{inc}}, \quad (18)$$

where we used  $R = |\mathbf{R}|$  and the following definitions

$$\boldsymbol{\tau}_{\text{rem}} = \mathbf{1} - \hat{\mathbf{R}}\hat{\mathbf{R}},$$

$$\mathbf{R}'(\theta) = \begin{vmatrix} 1 + R_m(\theta) & 0 & 0 \\ 0 & 1 + R_m(\theta) & 0 \\ 0 & 0 & 1 + R_c(\theta) \end{vmatrix} \quad (19)$$

To calculate next the intensities is the standard procedure

$$I_{\text{rem}}(\mathbf{R}) = \frac{1}{2} \mathbf{E}_{\text{rem}}^*(\mathbf{R}) \cdot \mathbf{E}_{\text{rem}}(\mathbf{R}) \quad (20)$$

The expression is valid of course except for the specular beam direction

## 5. Discussion

Expressions (19) and (20) predict the Rayleigh scattered intensity produced by a large molecule on top of a dielectric surface, as can be measured. To our opinion the initial stages of the formation of polysilanes made by means of HOMOCVD on top of a cleavage plane of crystalline silicon, come close to such a description. As such this theory can be seen, after incorporation of the proper statistics, as a first-order approximation of the scattered intensity for that case. Predicted and measured intensities should match in an absolute way. Especially the polarization-dependent observations yield useful information. Taking into account however the existing experience about light-scattering from gaseous alkanes, it is sure that for adequate matching of theoretical and experimental intensities or depolarization ratios  $\epsilon_s$  has to be tuned around 10 and depending upon the type of adsorption  $\epsilon_r$  should be given a value of 1 (physisorption) or higher (chemisorption). If matching results, it learns us that the optical behaviour of covalently bonded

materials, especially silicon is properly described by means of a screened induced-dipole model. This would pave the way for reliable calculations of the optical response of more complicated silicon-based configurations.

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