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A new approach based on transfer matrix formalism to characterize porous silicon layers by reflectometry

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We use reflectometry coupled to transfer matrix formalism in order to investigate the comparative effect of surface (localized) and volume (distributed) losses inside a porous silicon monolayer. Both are modeled as fictive absorption. Surface losses are described as a Dirac-like singularity of permittivity localized at an interface whereas volume losses are described trough the imaginary part of the porous silicon complex permittivity. A good agreement with experimental data is determined by this formalism.

1 Introduction

Porous Silicon (PS) can be used as a base material for passive or active optical devices such as waveguides [1], Bragg reflectors and micro-cavities [2, 3] for optoelectronic-integrated devices or sensor applications. The parameters of thin films such as optical thickness are usually determined by reflectometry. Since both surface and volume losses are known to affect the reflection spectrum, it is important to take them into account properly. This is sometimes done through an overall fictive absorption coefficient in the porous layers [4], but in that case no difference is made between the distributed contribution due to volume scattering, and the localized contribution, which stems from the roughness of the interface under consideration: the fictive attenuation coefficient should be recalculated for any change of the physical thickness *d*.

The specific contribution of the interface has been considered in Ref. [5], where generalised Fresnel-like coefficients are derived in the frame of a diffractive model.

In what follows, we propose a somewhat simpler approach based exclusively on transfer matrix formalism, where localized losses are explicitly distinguished from distributed losses, under the form of a Dirac-like singularity of absorption exactly located at one interface (at least). Our method is illustrated on the specific example of a PS monolayer on a Si substrate.

2 Experimental set-up

The PS layers were obtained by anodisation of a highly doped p-type (100) silicon substrate. The electrolyte was composed of HF(50%):H_2O:ethanol (2-1-2). The porosity of the single layer (60 or 65%) was

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fixed by the applied current density (respectively 50 and 80 mA/cm^2). The process was followed by a brief plasma etching in order to remove the surperficial parasitic film [6].
The single layers have been characterized by means of UV-VIS-NIR spectroscopy. The reflectance spectra have been obtained by a LAMBDA 900 Perkin Elmer beam spectrometer equipped with a Specular Reflectance module at a $\theta_0 = 6°$ fixed angle that allows total reflection of the incident beam [Fig. 1]. Since we work in the vicinity of normal incidence, the measurement is almost insensitive to the state of polarization.

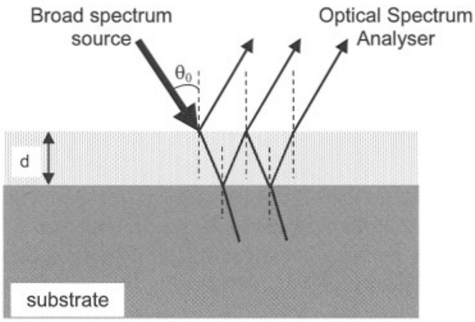

Fig. 1 Experimental set-up. The optical thickness (*nd*) of the sample depends on the porosity factor *p*; the angle of incidence is $\theta_0 = 6°$, small enough to neglect the difference of reflection coefficients between both states of polarization *s* (TE) and *p* (TM).

3 Modeling

While the position of reflective interference fringes is directly related to the optical thickness of the monolayer, their contrast is also due to the overall losses. The volume losses inside the PS are described through the imaginary part of its complex permittivity $\varepsilon_{PS} = \varepsilon_{Br} - i\,\varepsilon''_{vs}$, where ε_{Br} is deduced from the permittivity ε_S of intrinsic Si [7] and the porosity p through the Bruggeman model [8], while ε''_{vs} represents volume scattering. Surface losses are represented by a Dirac-like singularity of the dielectric permittivity [9], located at the PS/substrate interface and, if needed, at the air/PS interface.
Let us begin with the simplest model, where surface losses are assumed located on the PS/substrate interface only. For TE polarization, the transfer matrix [M] reads:

$$[M] = \begin{bmatrix} \frac{k_1+k_2}{2k_1} & \frac{k_1-k_2}{2k_1} \\ \frac{k_1-k_2}{2k_1} & \frac{k_1+k_2}{2k_1} \end{bmatrix} \begin{bmatrix} \exp(+ik_2 d) & 0 \\ 0 & \exp(-ik_2 d) \end{bmatrix} \begin{bmatrix} \frac{k_2+k_3+K''}{2k_2} & \frac{k_2-k_3+K''}{2k_2} \\ \frac{k_2-k_3-K''}{2k_2} & \frac{k_2+k_3-K''}{2k_2} \end{bmatrix} \tag{1}$$

where $k_1 = n_0\,(\omega/c)\cos(\theta_0)$, $k_{//} = n_0\,(\omega/c)\sin(\theta_0)$, $k_2 = [\varepsilon_{PS}\,(\omega/c)^2 - k_{//}^2]^{1/2}$, $k_3 = [\varepsilon_S\,(\omega/c)^2 - k_{//}^2]^{1/2}$ are the wavevector in the air (of refractive index n_0), in the monolayer (of thickness d) and in the substrate, while the real positive parameter K'' represents losses localized at the interface. In Eq. (1), the Dirac-like singularity appears through K'' in the generalized interface matrix, whereas the distributed losses are essentially represented by Im[$k_2 d$] in the central propagation matrix. The time dependence is taken as $\exp(+i\,\omega\,t)$.
The reflection $R = |M_{21}/M_{11}|^2$ is a function of the (frequency-dependent) elements M_{np} of the transfer matrix [M]. A straightforward calculation leads to the following expressions:

$$M_{11} = [(k_1+k_2)(k_2+k_3+K'')\exp(i\,k_2 d) + (k_1-k_2)(k_2-k_3-K'')\exp(-i\,k_2 d)]\,/\,(4\,k_1\,k_2), \tag{2a}$$

$$M_{21} = [(k_1-k_2)(k_2+k_3+K'')\exp(i\,k_2 d) + (k_1+k_2)(k_2-k_3-K'')\exp(-i\,k_2 d)]\,/\,(4\,k_1\,k_2). \tag{2b}$$

The reflection coefficient $r = M_{21}/M_{11}$ of the monolayer (in complex amplitude) can be expressed as:

$$r = \frac{r_A + r_B\exp[2\,\mathrm{Im}(k_2 d)]\exp[-2i\,\mathrm{Re}(k_2 d)]}{1 + r_A r_B\exp[2\,\mathrm{Im}(k_2 d)]\exp[-2i\,\mathrm{Re}(k_2 d)]}, \tag{3a}$$

where r_A (resp. r_B) denotes the reflection coefficient of the air/PS (resp. PS/substrate) interface:

$$r_A = \frac{k_1 - k_2}{k_1 + k_2}, \quad (3b) \qquad r_B = \frac{k_2 - k_3 - K''}{k_2 + k_3 + K''}. \quad (3c)$$

Note that the reflection r_B of the PS/substrate appears also "screened" by the losses that occur during the propagation along the PS layer, as represented by the term $\exp[2\,\mathrm{Im}(k_2 d)]$.
A simpler expression is sometimes used, when the overall reflection is seen as a two-wave interference (TWI) between the reflections on both interfaces:

$$r_{twi} = r_A + t_A\, t_A'\, r_B \exp[2\,\mathrm{Im}(k_2 d)] \exp[-2\,i\,\mathrm{Re}(k_2 d)], \quad (4a)$$

$$t_A t_A' = \frac{4 k_1 k_2}{(k_1 + k_2)^2}, \quad (4b)$$

$$R_{twi} = (R_1 + R_2)\,\{\,1 + V_0 \cos(\Phi)\,\}, \quad (4c)$$

$$R_1 = |r_A|^2, \qquad R_2 = |\,t_A\, t_A'\, r_B \exp[2\,\mathrm{Im}(k_2 d)]\,|^2, \quad (4d)$$

$$V_0 = 4\,(R_1 R_2)^{1/2}/(R_1 + R_2), \qquad \Phi = 2\,\mathrm{Re}(k_2 d). \quad (4e)$$

Nevertheless, for all its simplicity, this expression fails to take into account properly the multiple-path resonance inside the cavity.
The situation is barely more complex if surface losses are taken into account at both interfaces. For TE polarization, the transfer matrix [M] reads:

$$[M] = \begin{bmatrix} \frac{k_1 + k_2 + K'}{2k_1} & \frac{k_1 - k_2 + K'}{2k_1} \\ \frac{k_1 - k_2 - K'}{2k_1} & \frac{k_1 + k_2 - K'}{2k_1} \end{bmatrix} \begin{bmatrix} \exp(+ik_2 d) & 0 \\ 0 & \exp(-ik_2 d) \end{bmatrix} \begin{bmatrix} \frac{k_2 + k_3 + K''}{2k_2} & \frac{k_2 - k_3 + K''}{2k_2} \\ \frac{k_2 - k_3 - K''}{2k_2} & \frac{k_2 + k_3 - K''}{2k_2} \end{bmatrix}, \quad (5)$$

where K' (resp. K'') stands for losses at the first (resp. the second) interface.

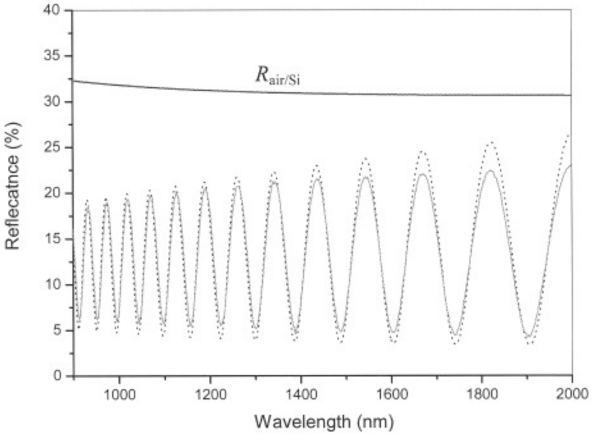

Fig. 2 Experimental (straight line) and theoretical (dotted line) reflection spectra for a sample of thickness $d \approx 5.46$ µm and porosity $p = 0.6$, with volume scattering given by $\varepsilon''_{vs} = 0.045$ and the same localized losses at both interfaces ($K' = K'' = 8.10^{-4}$ rad.nm^{-1}). The Fresnel reflection air/Si is also drawn for reference ($R_{air/Si}$).

4 Experimental results and discussion

As far as our sample is concerned, we found realistic to assume the same losses at both interfaces ($K' = K''$). Theoretical and experimental spectra are reported in Fig. 2. A good agreement with experimental spectrum is observed by fitting the parameters (porosity, thickness, ε''_{vs} and $K' = K''$) despite of a high value ε''_{vs}. The values of porosity and thickness are verified experimentally.

It should be noted that with $p = 0.6$, the theoretical visibility factor of the fringes $V_0 = (R_{MAX} - R_{min})/(R_{MAX} + R_{min})$ is almost equal to 1, since the index n_{PS} of the monolayer ensures that both interfaces (air/PS and PS/Si) exhibit almost the same reflection. As expected, the experimental visibility factor V_{exp} is slightly lower, most notably because of the interface waviness (responsible for fringe blurring, see Section 5 below).

Nevertheless, this description leaves some theoretical as well as physical problems to be addressed. As a matter of fact, the surface scattering losses could also be represented as a small intermediary layer exhibiting absorption, located symmetrically around the interface. The two approaches are depicted schematically in Fig. 3. Oddly enough, the structural behavior of both configurations appears very different. An absorbing layer of finite (albeit arbitrary small) size leads necessarily to a screening of the interface reflection, whatever the order of the indices. On the other hand, a Dirac-like singularity located exactly at the interface exhibits an extra reflection for the incident wave coming from the least refringent medium.

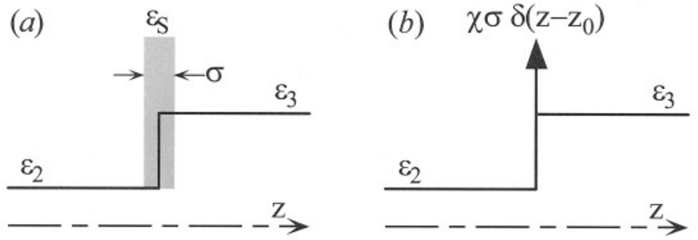

Fig. 3 Two different ways of modeling surface scattering at the PS/substrate interface. Oddly enough, even when matched so that transmission is affected the same way in both cases, the two models predict different behaviors in reflection: in case (a) both R_{23} and R_{32} are reduced, whereas in case (b), R_{23} is slightly enhanced due to an extra reflection on the singularity.

In the case of a small absorbing layer of finite size, the transfer matrix takes the following form:

$$[M] = \begin{bmatrix} \frac{k_1 + k_2}{2k_1} & \frac{k_1 - k_2}{2k_1} \\ \frac{k_1 - k_2}{2k_1} & \frac{k_1 + k_2}{2k_1} \end{bmatrix} \begin{bmatrix} \exp(+ik_2 d) & 0 \\ 0 & \exp(-ik_2 d) \end{bmatrix} \begin{bmatrix} \frac{k_2 + k_3}{2k_2}\exp(S) & \frac{k_2 - k_3}{2k_2} \\ \frac{k_2 - k_3}{2k_2} & \frac{k_2 + k_3}{2k_2}\exp(-S) \end{bmatrix}, \tag{6}$$

where S represents the localized scattering losses. This equation, that should be compared with Eq. (1), means that all reflection and transmission coefficients (in complex amplitude) of the PS/substrate interface are reduced as $\exp(-S)$, whatever the direction of propagation of the incident wave. This approach is consistent with the approximation sometimes used for describing roughness effects in Molecular Beam Epitaxy [10, 11]. The same treatment can be extended to the first air/PS interface.

5 Influence of waviness

Because of the waviness [12] affecting the monolayer, the contrast of interference fringes that can be experimentally measured appears lower than the theoretical one. This can be easily understood by considering the fluctuation δd around the nominal thickness d. It seems realistic to assume that this fluctuation is well described by a Gaussian distribution $G(\delta d)$ of null mean value and root mean square (rms) a.

For the sake of illustration, let us restrict ourselves to the two-wave interference approximation. Instead of Eq. (4c), the experimentally measured signal is blur0red according to:

$$R_{twi\_exp} = (R_1 + R_2) \int \{ 1 + V_0 \cos[2\,\mathrm{Re}(k_2)(d + \delta d)] \}\, G(\delta d)\, d(\delta d). \tag{7a}$$

A straightforward calculation leads to:

$$R_{twi\_exp} = (R_1 + R_2)\ \{\ 1 + V_{exp} \cos(\Phi)\ \}, \qquad (7b)$$

with the same spectral period and average reflection $(R_1 + R_2)$, but a visibility factor V_{exp} instead of V_0:

$$V_{exp} = V_0\ \hat{G}(a), \qquad (7c)$$

where $\hat{G}(a)$ represents the Fourier Transform of $G(\delta d)$. The greater the rms a of the thickness fluctuation, the lower the experimental visibility factor V_{exp}. We would like to emphasize that such a blurring does *not* affect the average reflection $(R_1 + R_2)$; only the extremal values are changed:

R_{min} is increased from $(R_1^{1/2} - R_2^{1/2})^2 = (R_1 + R_2)\ \{\ 1 - V_0\ \}$ to $(R_1 + R_2)\ \{\ 1 - V_{exp}\ \}$,

R_{MAX} is decreased from $(R_1^{1/2} + R_2^{1/2})^2 = (R_1 + R_2)\ \{\ 1 + V_0\ \}$ to $(R_1 + R_2)\ \{\ 1 + V_{exp}\ \}$.

Beyond the TWI approximation, the effect of waviness on the reflection spectrum can be thought as a convolution of the nominal curve $R(\omega)$ by an experimental Point Spread Function (PSF). Actually, the finite extension of the latter results from many factors: not only thickness fluctuation, but also index fluctuation, finite numerical aperture, and intrinsic resolution of the spectrometer.

6 Conclusions

We have presented a new transfer matrix approach to the experimental study of a porous silicon monolayer on a Si substrate, where surface scattering losses (either at the PS/substrate interface or at both interfaces) are modeled as a Dirac-like singularity of absorption. This enables one to consider separately losses coming from volume scattering inside the monolayer and losses located at the interface.
This approach should be compared with another model where surface scattering losses are represented as a arbitrarily thin absorbing layer, symmetrically disposed around the same interface. Oddly enough, in spite of their conceptual similarity, both models do not predict the same behavior as far as reflection coefficients are concerned. Besides, neither of them seems to agree with a calculation proposed in Ref. [5]. Obviously, more experimental as well as theoretical work remains to be done.

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