POTENTIAL MODULATION ON TOTAL INTERNAL REFLECTION ELLIPSOMETRY

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This supporting information provides the detailed deduction of eqs. (1) and (9).

THE FRACTIONAL CHANGE $\delta I/I$

For conventional PCSA configuration, the fractional change $\delta I/I$ of the optical response δI is given by

$$\frac{\delta I}{I} = \frac{\delta \boldsymbol{R}_s}{\boldsymbol{R}_s} + \alpha'_1\delta\psi + \alpha'_2\delta\Delta \qquad \text{(s-1)}$$

where $\boldsymbol{R}_s$ is the reflectance of the surface for s-polarized light, given by

$$\boldsymbol{R}_s = |R_s|^2$$

α'_1 and α'_2 are the ellipsometric parameter coefficients, given by

$$\alpha'_1 = \frac{2[\tan\bar{\psi}(1+\cos 2A) - \sin 2A\sin(2P+\bar{\Delta})]}{[1-\cos 2\bar{\psi}\cos 2A + \sin 2\bar{\psi}\sin(2P+\bar{\Delta})\sin 2A]}$$

$$\alpha'_2 = \frac{-\sin 2\bar{\psi}\cos(2P+\bar{\Delta})\sin 2A}{[1-\cos 2\bar{\psi}\cos 2A + \sin 2\bar{\psi}\sin(2P+\bar{\Delta})\sin 2A]}$$

Besides, $\delta\boldsymbol{R}_s/\boldsymbol{R}_s$, $\delta\boldsymbol{R}_p/\boldsymbol{R}_p$ and $\delta\psi$ are interrelated by

$$\frac{\delta\boldsymbol{R}_p}{\boldsymbol{R}_p} = \frac{\delta\boldsymbol{R}_s}{\boldsymbol{R}_s} + \frac{4\delta\psi}{\sin 2\psi} \qquad \text{(s-2)}$$

Taking eq. (s-2) into eq. (s-1), we obtain eq. (1), where $\alpha_1 = \alpha'_1 - \frac{4}{\sin 2\psi}$ and $\alpha_2 = \alpha'_2$.

THE DIELECTRIC CONSTANT CHANGES ON ρ

To discuss the relationship between the dielectric constant variations and ellipsometric parameters taking logarithmic differential of $\rho = R_p/R_s$, we have

$$\frac{\delta\rho}{\rho} = \frac{\delta R_p}{R_p} - \frac{\delta R_s}{R_s} \qquad \text{(s-3)}$$

let

$$R_\nu = \frac{N_\nu}{D_\nu} \qquad \text{(s-4)}$$

where ν represents p-polarization when $\nu = p$ and s-polarization when $\nu = s$. In eq. (s-4),

$$N_\nu = r_{01\nu} + r_{12\nu}X,\ D_\nu = 1 + r_{01\nu}r_{12\nu}X \qquad \text{(s-5)}$$

and

$$X = exp(2j\beta) \qquad \text{(s-6)}$$

where $r_{01\nu}$ and $r_{12\nu}$ are Fresnel coefficients at 0-1 interface and 1-2 interface and β is the interface phase change coefficient. The explicit expressions can be seen in [28].

Taking logarithmic differential of eq. (s-4), we get

$$\frac{\delta R_\nu}{R_\nu} = \frac{\delta N_\nu}{N_\nu} - \frac{\delta D_\nu}{D_\nu} \qquad \text{(s-7)}$$

And

$$\delta N_\nu = \delta r_{01\nu} + X\delta r_{12\nu} + r_{12\nu}\delta X \qquad \text{(s-8)}$$

$$\delta D_\nu = r_{12\nu}X\delta r_{01\nu} + r_{01\nu}X\delta r_{12\nu} + r_{01\nu}r_{12\nu}\delta X \qquad \text{(s-9)}$$

Taking eqs. (s-8) and (s-9) into eq. (s-7), we have

$$\frac{\delta R_\nu}{R_\nu} = \left(\frac{1}{N_\nu} - \frac{r_{12\nu}X}{D_\nu}\right)\delta r_{01\nu} + \left(\frac{1}{N_\nu} - \frac{r_{01\nu}}{D_\nu}\right)X\delta r_{12\nu} + \left(\frac{1}{N_\nu} - \frac{r_{01\nu}}{D_\nu}\right)r_{12\nu}\delta X \qquad \text{(s-10)}$$

Eq. (s-10) suggests the modulation of ν -polarized reflected light can be divided into three parts: the Fresnel coefficient modulations at 0-1 and 1-2 interfaces and the phase change modulation when the light passes through the film.

On the other hand, we have

$$\delta r_{01p} = \frac{2n_0 \cos\phi_0 \cos 2\phi_1}{(n_1 \cos\phi_0 + n_0 \cos\phi_1)^2 \cos\phi_1} \delta n_1 \quad \text{(s-11)}$$

$$\delta r_{12p} = -\frac{2n_2 \cos\phi_2 \cos 2\phi_1}{(n_2 \cos\phi_1 + n_1 \cos\phi_2)^2 \cos\phi_1} \delta n_1 + \frac{2n_1 \cos\phi_1 \cos 2\phi_2}{(n_2 \cos\phi_1 + n_1 \cos\phi_2)^2 \cos\phi_2} \delta n_2 \quad \text{(s-12)}$$

$$\delta r_{01s} = -\frac{2n_0 \cos\phi_0}{(n_0 \cos\phi_0 + n_1 \cos\phi_1)^2 \cos\phi_1} \delta n_1 \quad \text{(s-13)}$$

$$\delta r_{12p} = \frac{2n_2 \cos\phi_2}{(n_1 \cos\phi_1 + n_2 \cos\phi_2)^2 \cos\phi_1} \delta n_1 - \frac{2n_1 \cos\phi_1}{(n_1 \cos\phi_1 + n_2 \cos\phi_2)^2 \cos\phi_2} \delta n_2 \quad \text{(s-14)}$$

Or in terms of dielectric constant ε:

$$\delta r_{01p} = L_{01p} \delta\varepsilon_1 \quad \text{(s-15)}$$

$$\delta r_{12p} = L_{12p} \delta\varepsilon_1 + M_{12p} \delta\varepsilon_2 \quad \text{(s-16)}$$

$$\delta r_{01s} = L_{01s} \delta\varepsilon_1 \quad \text{(s-17)}$$

$$\delta r_{12s} = L_{12s} \delta\varepsilon_1 + M_{12s} \delta\varepsilon_2 \quad \text{(s-18)}$$

where

$$L_{01p} = \frac{\sqrt{\varepsilon_0} \cos\phi_0 \cos 2\phi_1}{\sqrt{\varepsilon_1} \cos\phi_1 \left(\sqrt{\varepsilon_1} \cos\phi_0 + \sqrt{\varepsilon_0} \cos\phi_1\right)^2} \quad \text{(s-19)}$$

$$L_{12p} = -\frac{\sqrt{\varepsilon_2} \cos\phi_2 \cos 2\phi_1}{\sqrt{\varepsilon_1} \cos\phi_1 (\sqrt{\varepsilon_2} \cos\phi_1 + \sqrt{\varepsilon_1} \cos\phi_2)^2} \quad \text{(s-20)}$$

$$M_{12p} = \frac{\sqrt{\varepsilon_1} \cos\phi_1 \cos 2\phi_1}{\sqrt{\varepsilon_2} \cos\phi_2 (\sqrt{\varepsilon_2} \cos\phi_1 + \sqrt{\varepsilon_1} \cos\phi_2)^2} \quad \text{(s-21)}$$

$$L_{01s} = -\frac{\sqrt{\varepsilon_0}\, cos\, \phi_0}{\sqrt{\varepsilon_1}\, cos\, \phi_1 \left(\sqrt{\varepsilon_0}\, cos\, \phi_0 + \sqrt{\varepsilon_1}\, cos\, \phi_1\right)^2} \quad \text{(s-22)}$$

$$L_{12s} = \frac{\sqrt{\varepsilon_2}\, cos\, \phi_2}{\sqrt{\varepsilon_1}\, cos\, \phi_1 (\sqrt{\varepsilon_1}\, cos\, \phi_1 + \sqrt{\varepsilon_2}\, cos\, \phi_2)^2} \quad \text{(s-23)}$$

$$M_{12s} = -\frac{\sqrt{\varepsilon_1}\, cos\, \phi_1}{\sqrt{\varepsilon_2}\, cos\, \phi_2 (\sqrt{\varepsilon_1}\, cos\, \phi_1 + \sqrt{\varepsilon_2}\, cos\, \phi_2)^2} \quad \text{(s-24)}$$

And

$$\delta X = -2jX\delta\beta = \gamma X \delta\varepsilon_1 \quad \text{(s-25)}$$

where

$$\gamma = -j \frac{4\pi^2}{\beta} \left(\frac{d_1}{\lambda}\right)^2 \quad \text{(s-26)}$$

For a given glass/Au/electrolyte system, L_{01p}, L_{12p}, M_{12p}, L_{01s}, L_{12s}, M_{12s}, γ and X are the functions of the angle of incidence, ϕ_0.

According to eq. (s-10), we obtain

$$\frac{\delta R_\nu}{R_\nu} = Q_\nu \delta\varepsilon_1 + P_\nu \delta\varepsilon_2 \quad \text{(s-27)}$$

where

$$Q_\nu = \left(\frac{1}{r_{01\nu} + r_{12\nu} X} - \frac{r_{12\nu} X}{1 + r_{01\nu} r_{12\nu} X}\right) L_{01\nu}$$

$$+\left(\frac{1}{r_{01\nu}+r_{12\nu}X}-\frac{r_{01\nu}}{1+r_{01\nu}r_{12\nu}X}\right)XL_{12\nu}$$

$$+\left(\frac{1}{r_{01\nu}+r_{12\nu}X}-\frac{r_{01\nu}}{1+r_{01\nu}r_{12\nu}X}\right)\gamma r_{12\nu}X \quad \text{(s-28)}$$

$$P_\nu=\left(\frac{1}{r_{01\nu}+r_{12\nu}X}-\frac{r_{01\nu}}{1+r_{01\nu}r_{12\nu}X}\right)XM_{12\nu} \quad \text{(s-29)}$$

Taking eqs. (s-27), (s-28) and (s-29) into (s-3), we have eq. (9). The explicit expression of κ_1 and κ_2 is given by

$$\kappa_1=Q_p-Q_s$$

$$=\left(\frac{1}{r_{01p}+r_{12p}X}-\frac{r_{12p}X}{1+r_{01p}r_{12p}X}\right)L_{01p}+\left(\frac{1}{r_{01p}+r_{12p}X}-\frac{r_{01p}}{1+r_{01p}r_{12p}X}\right)XL_{12p}$$

$$+\left(\frac{1}{r_{01p}+r_{12p}X}-\frac{r_{01p}}{1+r_{01p}r_{12p}X}\right)\gamma r_{12p}X-\left(\frac{1}{r_{01s}+r_{12s}X}-\frac{r_{12s}X}{1+r_{01s}r_{12s}X}\right)L_{01s}$$

$$-\left(\frac{1}{r_{01s}+r_{12s}X}-\frac{r_{01s}}{1+r_{01s}r_{12s}X}\right)XL_{12s}-\left(\frac{1}{r_{01s}+r_{12s}X}-\frac{r_{01s}}{1+r_{01s}r_{12s}X}\right)\gamma r_{12s}X \quad \text{(s-30)}$$

$$\kappa_2=P_p-P_s=\left(\frac{1}{r_{01\nu}+r_{12\nu}X}-\frac{r_{01\nu}}{1+r_{01\nu}r_{12\nu}X}\right)XM_{12\nu}-\left(\frac{1}{r_{01\nu}+r_{12\nu}X}-\frac{r_{01\nu}}{1+r_{01\nu}r_{12\nu}X}\right)XM_{12\nu} \quad \text{(s-31)}$$