POTENTIAL MODULATION ON TOTAL INTERNAL REFLECTION ELLIPSOLOGY

Wei Liu, †, ‡, ¶, ⊥ Yu Niu, †, ‡, ⊥ A. S. Viana, ‡ Jorge P. Correia, § and Gang Jin*, †, ‡

†NML, Institute of Mechanics, Chinese Academy of Sciences, # 15, Bei-si-huan West Road, Beijing, 100190, China
‡ Beijing Key Laboratory of Engineered Construction and Mechanobiology, Institute of Mechanics, Chinese Academy of Sciences, 15 Bei-si-huan West Road, Beijing 100190, China
¶ University of Chinese Academy of Sciences, # 19, Yu-quan Road, Beijing, 100049, China
§ Centro de Química e Bioquímica, Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal
⊥ Contributed equally to this work

Email: gajin@imech.ac.cn
Fax: +86-10-82544138

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 \( \delta I \) is given by

\[
\frac{\delta I}{I} = \frac{\delta R_s}{R_s} + \alpha_1' \delta \psi + \alpha_2' \delta \Delta
\]  

(s-1)

where \( R_s \) is the reflectance of the surface for s-polarized light, given by

\[
R_s = |R_s|^2
\]

\( \alpha_1' \) and \( \alpha_2' \) are the ellipsometric parameter coefficients, given by

\[
\alpha_1' = \frac{2[\tan \psi(1 + \cos 2A) - \sin 2A \sin (2P + \Delta)]}{[1 - \cos 2\psi \cos 2A + \sin 2\psi \sin (2P + \Delta) \sin 2A]} - \frac{\sin 2\psi \cos (2P + \Delta) \sin 2A}{[1 - \cos 2\psi \cos 2A + \sin 2\psi \sin (2P + \Delta) \sin 2A]}
\]

\( \alpha_2' \) represents the phase change coefficient. The explicit expressions can be seen in \( s^8 \).

Besides, \( \delta R_s/R_s, \delta R_p/R_p \) and \( \delta \psi \) are interrelated by

\[
\frac{\delta R_p}{R_p} = \frac{\delta R_s}{R_s} + \frac{4\delta \psi}{\sin 2\psi}
\]  

(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 \( \rho \)

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

\[
\frac{\delta \rho}{\rho} = \frac{\delta R_p}{R_p} - \frac{\delta R_s}{R_s}
\]  

(s-3)

let

\[
R_v = \frac{N_v}{\delta v}
\]  

(s-4)

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

\[
N_v = r_{01v} + r_{12v} X, \quad D_v = 1 + r_{01v} r_{12v} X
\]  

(s-5)

and

\[
X = \exp(2j\beta)
\]  

(s-6)

where \( r_{01v} \) and \( r_{12v} \) are Fresnel coefficients at 0-1 interface and 1-2 interface and \( \beta \) is the interface phase change coefficient. The explicit expressions can be seen in \( s^8 \).

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

\[
\frac{\delta N_v}{N_v} = \frac{\delta r_{01v}}{r_{01v}} + X \frac{\delta r_{12v}}{r_{12v}} + r_{12v} \delta X
\]  

(s-7)

And

\[
\delta N_v = \delta r_{01v} + X \delta r_{12v} + r_{12v} \delta X
\]  

(s-8)

\[
\delta D_v = r_{12v} X \delta r_{01v} + r_{01v} X \delta r_{12v} + r_{01v} r_{12v} \delta X
\]  

(s-9)

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

\[
\frac{\delta N_v}{N_v} = \left( \frac{1}{N_v} - \frac{r_{12v} X}{N_v} \right) \delta r_{01v} + \left( \frac{1}{N_v} - \frac{r_{12v}}{N_v} \right) X \delta r_{12v} + \left( \frac{1}{N_v} - \frac{r_{01v}}{N_v} \right) r_{12v} \delta X
\]  

(s-10)

Eq. (s-10) suggests the modulation of \( V \)-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

\[ \delta r_{12p} = -\frac{2n_2 \cos \phi_2 \cos 2\phi_1}{(n_2 \cos \phi_1 + n_1 \cos \phi_2)^2 \cos \phi_1} \delta n_1 + \frac{2n_1 \cos \phi_1 \cos 2\phi_2}{(n_2 \cos \phi_1 + n_1 \cos \phi_2)^2 \cos \phi_2} \delta n_2 \]  

(8-12)

Or in terms of dielectric constant \( \varepsilon \):

\[ \delta r_{12p} = L_{12p} \delta \epsilon_1 + M_{12p} \delta \epsilon_2 \]  

(8-16)

where

\[ L_{12p} = \frac{\sqrt{\epsilon_0} \cos \phi_1 (\sqrt{\epsilon_0} \cos \phi_0 + \sqrt{\epsilon_1} \cos \phi_2)}{\sqrt{\epsilon_1} \cos \phi_2 (\sqrt{\epsilon_1} \cos \phi_1 + \sqrt{\epsilon_1} \cos \phi_2)^2} \]  

(8-20)

And

\[ \delta X = -2jX \delta \beta = \gamma X \delta \epsilon_1 \]  

(8-25)

where

\[ \gamma = -\frac{4\pi^2 (\frac{d_s}{2})^2}{\rho} \]  

(8-26)

For a given glass/Au/electrolyte system, \( L_{01p}, L_{12p}, M_{12p}, L_{01s}, L_{12s}, M_{12s} \) \( \gamma \) and \( X \) are the functions of the angle of incidence, \( \phi_0 \).

According to eq. (8-10), we obtain

\[ \frac{\delta R_\nu}{R_\nu} = Q_\nu \delta \epsilon_1 + \nu \delta \epsilon_2 \]  

(8-27)

where

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

S-3
\[ P_v = \left( \frac{1}{r_{01v} + r_{12v}} - \frac{r_{01v}}{1 + r_{01v} r_{12v}} \right) X M_{12v} \]  

Taking eqs. (s-27), (s-28) and (s-29) into (s-3), we have eq. (9). The explicit expression of \( \kappa_1 \) and \( \kappa_2 \) is given by

\[ \kappa_1 = Q_p - Q_s \]

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

\[ + \left( \frac{1}{r_{01p} + r_{12p} X} - \frac{r_{01p}}{1 + r_{01p} r_{12p} X} \right) Y r_{12p} X + \left( \frac{1}{r_{01s} + r_{12s} X} - \frac{r_{12s} X}{1 + r_{01s} r_{12s} X} \right) L_{01s} \]

\[ - \left( \frac{1}{r_{01s} + r_{12s} X} - \frac{r_{01s}}{1 + r_{01s} r_{12s} X} \right) X L_{12s} - \left( \frac{1}{r_{01s} + r_{12s} X} - \frac{r_{01s}}{1 + r_{01s} r_{12s} X} \right) Y r_{12s} X \]  

\[ \kappa_2 = P_p - P_s = \left( \frac{1}{r_{01v} + r_{12v} X} - \frac{r_{01v}}{1 + r_{01v} r_{12v} X} \right) X M_{12v} - \left( \frac{1}{r_{01v} + r_{12v} X} - \frac{r_{01v}}{1 + r_{01v} r_{12v} X} \right) X M_{12v} \]