Basic Primer on the details of modelling calculations

At a high level, we have modelled our system as a series of layers and applied the Fresnel equations to calculate reflectivity and transmissivity as a function of angle or frequency. First, all of the layers have to be defined and assigned a permittivity function whether modelled or experimental. Modelled permittivity functions may be fixed values (frequency invariant), Drude-modelled (for conductors), Lorentz-modelled (for dielectrics), or others. For composite layers containing several interspersed materials, effective medium approximations (EMA, or equivalently, effective medium theory, EMT) may be used. Once permittivities are obtained for each layer, we use a matrix method developed by Ohta and Hatsuo[1] to apply the Fresnel equations and Snell's law to the system of layered materials and calculate the reflectivity and transmissivity.

Basic optical properties

Relative permittivity, ϵ, and complex refractive index, η, are two different ways of encoding the same information. One can convert between the two by: $\eta^2 = \mu\epsilon$, and for the cases considered in this work, the magnetic permeability, μ, equals unity.

The permittivity can be separated into real and imaginary components:

$$\eta = n + i\kappa \tag{1}$$
$$\epsilon = \eta^2 = (n + i\kappa)^2 = n^2 + 2in\kappa - \kappa^2 \tag{2}$$
$$\epsilon_1 = n^2 - \kappa^2 \tag{3}$$
$$\epsilon_2 = 2n\kappa \tag{4}$$

where $\epsilon_1$and $\epsilon_2$are the real and imaginary parts of the permittivity, respectively.

The various forms of expressing the wavelength/frequency of the electromagnetic radiation are explicitly given in Equation 5

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{c}{\nu} = \frac{2\pi c}{\omega} \tag{5}$$

where c is the speed of light in a vacuum.

Lorentz model

The absorbing organic molecule was modelled as a Lorentz oscillator:

$$\epsilon_{lorentz} = \epsilon_\infty + \frac{\omega_p^2}{\omega_r^2 - \omega^2 - i\omega\gamma} \tag{6}$$

where ϵ_∞ is the relative permittivity off-resonance (i.e. at very high frequency), ω_p is the angular plasma frequency, ω_r is the angular resonant frequency, ω is the angular frequency of the electric field driving the oscillator (i.e. angular frequency of the incident IR radiation), and γ is the damping factor of the molecular resonance.

Drude model

The permittivity values of metals and conductive metal oxides can be modelled using the Drude model. In this work, the Drude model was used as the function describing the permittivity of IZO films. Electrons in metals are unbound, and thus there is no restoring force causing them to oscillate at some resonant frequency. Therefore, the Drude model is given by the Lorentz model for the special case of $\omega_r = 0$:

$$\epsilon_{Drude} = \epsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\gamma} \qquad (7)$$

The plasma frequency, ω_p, is given by:

$$\omega_p = \left(\frac{Ne^2}{\epsilon_0 m^*}\right)^{\frac{1}{2}} \qquad (8)$$

where N is the free carrier concentration (density of conduction electrons), e is the elementary charge, ϵ_0 is the permittivity of free space, and m^* is the effective electron mass. The effective mass is a calculated value of an electron's *apparent* mass based on how the electron would be affected by forces applied to it.

Bruggeman Effective Medium Approximation

The permittivity function of the structured metal surface is not accurately described by the permittivity of the bulk metal. Various Effective Medium Approximations (EMAs) have been developed to model the permittivity of a composite structured layer. Examples include the Bruggeman, Maxwell-Garnett and Hunderi EMA models.[2]

In this work, we have followed Osawa[3] and used the Bruggeman EMA, which treats the surface as a collection of metal prolate spheroids in a host medium which fills the spaces between the metal particles. The particles may be coated by a thin uniform layer of some organic molecule. Thus, the Bruggeman EMA effectively combines the permittivity values of the three constituents (metal, organic molecule, host medium) to obtain an effective permittivity of the composite layer. This approximation is valid when the microstructural elements of the layer (in this case, the prolate spheroids) are much smaller than the wavelengths of IR light.

It is not entirely clear how the metal spheroids are arranged within the layer in Osawa's work, so this work assumes that the major semi-axes of the spheroids are parallel to the surface, and thus the layer has a thickness equal to the diameter of the minor semi-axis. Additionally, we assume that within this limitation, the prolate spheroids may adopt any possible rotation.

Granqvist[2] defines the Bruggeman EMA as:

$$\epsilon_{BR} = \frac{\epsilon_h\left(1 - F + \frac{1}{3}F\alpha\right)}{1 - F - \frac{2}{3}F\alpha} \qquad (9)$$

where ϵ_h is the permittivity of the host medium, F is the fractional volume of the layer occupied by metal particles, and α is the polarizability factor of the particles.

The polarizability, α, is a function of the volume ratio of the uncoated to coated particles (Q), the depolarization factors of the core and coated prolate particles (L_1, L_2), and also the permittivity of the metal (ϵ_m) and the dielectric coating (ϵ_d):

$$\alpha = \frac{(\epsilon_d - \epsilon_{BR})[\epsilon_m L_1 + \epsilon_d(1-L_1)] + Q(\epsilon_m - \epsilon_d)[\epsilon_d(1-L_1) + \epsilon_{BR} L_2]}{[\epsilon_d L_2 + \epsilon_{BR}(1-L_1)][\epsilon_m L_1 + \epsilon_d(1-L_1)] + Q(\epsilon_m - \epsilon_d)(\epsilon_d - \epsilon_{BR}) L_2 (1-L_2)} \tag{10}$$

Notice that the Bruggeman permittivity function is a parameter of the polarizability function. Solving eqn (9) for α and then setting the result equal to eqn (10) gives:

$$\frac{3(\epsilon_h - F\epsilon_h + F\epsilon_{BR} - \epsilon_{BR})}{-F(2\epsilon_{BR} + \epsilon_h)} = \frac{(\epsilon_d - \epsilon_{BR})[\epsilon_m L_1 + \epsilon_d(1-L_1)] + Q(\epsilon_m - \epsilon_d)[\epsilon_d(1-L_2) + \epsilon_{BR} L_2]}{[\epsilon_d L_2 + \epsilon_{BR}(1-L_2)][\epsilon_m L_1 + \epsilon_d(1-L_1)] + Q(\epsilon_m - \epsilon_d)(\epsilon_d - \epsilon_{BR}) L_2 (1-L_2)}. \tag{11}$$

It is possible to solve this equation for the Bruggeman permittivity, ϵ_{BR}, but the expression is very lengthy, and is not given here.

To calculate an absorbance spectrum, the Bruggeman permittivity must be also calculated in the absence of the dielectric coating (analyte film.) To calculate the Bruggeman permittivity of a film without dielectric coating, we replaced ϵ_d with ϵ_h.

Prolate ellipsoids are a class of spheroids with dimensions *a*, *b*, *c* where *b* = *c* and *a* > *b*, (*i.e.* where *a* is the major semi-axis, and *b*, *c* are the minor semi-axes). The one-dimensional depolarization factors for major and minor semi-axes of prolate spheroids are given by equations 4.2 and 4.3 in Stoner[4] (also equations 2.10 and 2.11 in Osborn[5]):

$$L_{major} = \frac{1}{m^2-1}\left[\frac{m}{(m^2-1)^{\frac{1}{2}}} \ln\left\{m + (m^2-1)^{\frac{1}{2}}\right\} - 1\right] \tag{12}$$

$$L_{minor} = \frac{1}{2}(1 - L_{major}) \tag{13}$$

where m is the ratio of the long semi-axis to the short semi axis. The depolarization factors given above are only valid for prolate spheroids, the particles may be best modelled by some other geometric solid defined by its own unique depolarization factors but this was not explored in this work. Given our assumption that the particles can adopt any rotation about the axis normal to the surface, we assume a random distribution of rotational orientations, so the depolarization factor of an average particle is taken to be the arithmetic mean of the depolarization factors along the major and minor semi-axes:

$$L_{eff} = \frac{L_{major} - L_{minor}}{2} \tag{14}$$

Note that this assumption means that the "effective depolarization factor of the collective particles" is independent of direction of the electric field, that is to say the same for s- and p-polarized light.

Ohta's matrix method

Ohta and Hatsuo[1] described a method to calculate reflectivity and transmissivity of layered systems using propagation matrices and the Fresnel equations for reflection and transmission coefficients. For each interface in the layered system of interest, a matrix is defined:

$$C_j = \begin{pmatrix} e^{-i\delta_{j-1}} & r_j e^{-i\delta_{j-1}} \\ r_j e^{i\delta_{j-1}} & e^{i\delta_{j-1}} \end{pmatrix} \quad (15)$$

where r is the Fresnel reflection coefficient and δ_{j-1} is the phase shift of the wave after passing through the boundary between the *j*-th and the (*j*+1)-th layer with respect to the phase of the wave at the boundary between the (*j*-1)-th and the *j*-th layer:

$$\delta_{j-1} = 2\pi\nu\eta_{j-1}\cos\theta_{j-1}h_{j-1} \quad (16)$$

The subscripts refer to the layer, with *j*-1 referring to the layer on the near side of the interface, with respect to the direction of propagation.

The product of all C_j matrices gives a 2 by 2 matrix with elements:

$$\prod_{j=1}^{n} C_j = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix} \quad (17)$$

And the overall reflection and transmission coefficients across the entire layered system are given by:

$$r = \frac{c_{21}}{c_{11}} \quad (18)$$

$$t = \frac{1}{c_{11}} \prod_{j=1}^{n} t_j \quad (19)$$

The Fresnel transmission coefficients for *s*- and *p*-polarized light at the *j*-th interface, t_j, are given by[6]:

$$t_{js} = \frac{2\xi_{j-1}}{\xi_j + \xi_{j-1}} \quad (20)$$

$$t_{jp} = \frac{2\eta_j\eta_{j-1}\xi_{j-1}}{\xi_{j-1} + \xi_j} \quad (21)$$

where:

$$\xi_j = \left|\eta_j cos\theta_j\right| \quad (22)$$

Note that the expression for t_{js} in Ohta[1] is incorrect, as is the expression for t_{jp} in Hansen.[6] Expressing the reflection coefficients in terms of ξ_j (*i.e.* forcing the real and imaginary components of the product $\eta_j cos\theta_j$ to both be positive) gives the correct root, causing the evanescent wave to decay exponentially as a function of distance from the terminal interface, which is the correct behaviour. If ξ_j is not in quadrant I of the complex plane, the evanescent wave will increase exponentially.

The observable quantities are reflectance (R) and transmittance (T) which are the square moduli of their respective coefficients. However, the cross-sectional area of the beam changes upon refraction, so transmissivity is multiplied by a factor accounting for this change in beam size:

$$R = |r|^2 \tag{23}$$

$$T_s = Re\left(\frac{\eta_{m+1}\cos\theta_{m+1}}{\eta_0 cos\theta_0}\right)|t_s|^2 \tag{24}$$

$$T_p = Re\left(\frac{\eta^*_{m+1}\cos\theta_{m+1}}{\eta^*_0 cos\theta_0}\right)\left|t_p\right|^2 \tag{25}$$