Title	Optical reflectance of solution processed quasi-superlattice ZnO and Al-doped ZnO (AZO) channel materials
Author(s)	Buckley, Darragh; McCormack, Robert; O'Dwyer, Colm
Publication date	2017-03-24
Original citation	Buckley, D., McCormack, R. and O'Dwyer, C. (2017) 'Optical reflectance of solution processed quasi-superlattice ZnO and Al-doped ZnO (AZO) channel materials', Journal of Physics D - Applied Physics, 50, 16LT01 (7pp). doi:10.1088/1361-6463/aa6559
Type of publication	Article (peer-reviewed)
Link to publisher's version	http://dx.doi.org/10.1088/1361-6463/aa6559 Access to the full text of the published version may require a subscription.
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Item downloaded from	http://hdl.handle.net/10468/3894

Supplementary material for

Optical Reflectance of Solution Processed Quasi-Superlattice ZnO and Al-doped ZnO (AZO) Channel Materials

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Optical Constant Determination

The Fresnel equations define the behaviour of light as it moves between mediums that have differing refractive indices. Equations 1 and 2 are the Fresnel coefficients for the amplitudes of reflected and transmitted light at normal incident which travels from surrounding medium (n_0) to the thin film (n_1) while Eqns 3 and 4 are the same coefficients expect for light travelling from n_1 to n_0.

$$r_1 = \frac{n_0 - n_1}{n_0 + n_1} \qquad (1)$$

$$t_1 = \frac{2n_0}{n_0 + n_1} \qquad (2)$$

$$r_1' = \frac{n_1 - n_0}{n_1 + n_0} \qquad (3)$$

$$t_1' = \frac{2n_1}{n_0 + n_1} \qquad (4)$$

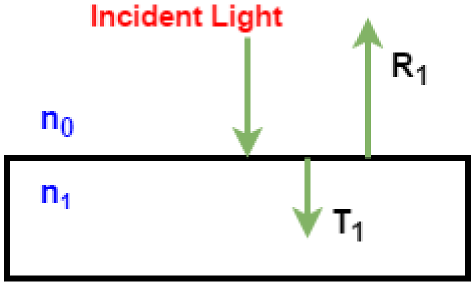

Figure S1: Reflection and transmission of incidence light on a smooth surface.

The amplitude of the reflected light (R) wave from the smooth surface interface is given by the following equation in terms the Fresnel reflection coefficients and the refractive indices (where $r_1' = -r_1$):

$$R = r_1 r_1' = \left(\frac{n_0 - n_1}{n_0 + n_1}\right)\left(\frac{n_0 - n_1}{n_1 + n_0}\right) = \left(\frac{n_0 - n_1}{n_0 + n_1}\right)^2 \quad (5)$$

Figure S2 below shows how light rays travel through a surrounding medium which is incident on a thin film layer (n_1) which has been deposited on a substrate (n_2) which is essentially a single layer thin film.

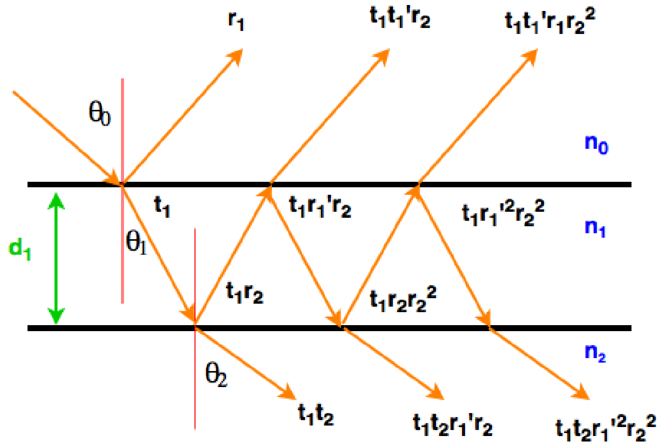

Figure S2: Light rays traveling through a single layer thin film.

The phase difference (δ_1) of the light which traverses through the single thin film layer of thickness d_1 is given by the equation:

Thus, the sum of the reflected amplitude of the incidence light is given by the equation:

$$\delta_1 = \left(\frac{2\pi}{\lambda}\right) n_1 d_1 \cos\theta_1 \quad (6)$$

$$R = r_1 + t_1 t_1' r_2 e^{-2i\delta_1} - t_1 t_1' r_1 r_2^2 e^{-4i\delta_1} + t_1 t_1' r_1^2 r_2^3 e^{-6i\delta_1} - t_1 t_1' r_1^3 r_2^4 e^{-8i\delta_1} + \cdots \quad (7)$$

$$\Rightarrow R = r_1 + \frac{t_1 t_1' r_2 e^{-2i\delta_1}}{1 + r_1 r_2 e^{-2i\delta_1}}$$

This expression above can be simplified further if the conservation of energy is applied and assuming the material is non-absorbing:

$$t_1 t_1' = 1 - r_1^2$$

Thus, Eqn 7 can now be written as:

$$\therefore \mathrm{R} = \frac{\mathrm{r}_1 + \mathrm{r}_2 \mathrm{e}^{-2\mathrm{i}\delta_1}}{1 + \mathrm{r}_1 \mathrm{r}_2 \mathrm{e}^{-2\mathrm{i}\delta_1}} \tag{8}$$

The ratio of the reflected energy (**R**) of the light to the incident energy of the light can now be determined. The value of **R** is given by the product of the amplitude of the reflected light wave with the complex conjugate of the amplitude of the reflected light wave:

$$\mathbf{R} = \mathrm{n}_0 \mathrm{RR}^* = \frac{\mathrm{n}_0(\mathrm{r}_1^2 + 2\mathrm{r}_1\mathrm{r}_2\cos 2\delta_1 + \mathrm{r}_2{}^2)}{1 + 2\mathrm{r}_1\mathrm{r}_2\cos 2\delta_1 + \mathrm{r}_1^2\mathrm{r}_2^2} \tag{9}$$

The reflectance in Eqn 9 above can be written as,

$$\mathbf{R} = \frac{\mathrm{A} + \mathrm{B}\cos C}{\mathrm{D} + \mathrm{B}\cos C} \tag{10}$$

where:

$\mathrm{A} = \mathrm{r}_1^2 + \mathrm{r}_2^2$ Assuming $\mathrm{n}_0 = 1$ (medium is air) $\mathrm{B} = 2\mathrm{r}_1\mathrm{r}_2$

$\mathrm{C} = 2\delta_1 = \left(\frac{4\pi}{\lambda}\right)\mathrm{n}_1\mathrm{d}_1$ Assuming angle of incidence $= 0°$ $\mathrm{D} = 1 + \mathrm{r}_1^2\mathrm{r}_2^2$

If the Fresnel coefficients for the amplitudes of reflected light at the medium thin film interface which is Eqn 1 and at the thin film substrate interface $\left[r_2 = \frac{n_1 - n_2}{n_1 + n_2}\right]$ are substituted into Eqn 10 above, the reflectance of a single layer thin film can be expressed as:

$$\mathbf{R} = \frac{\left(\frac{\mathrm{n}_0 - \mathrm{n}_1}{\mathrm{n}_0 + \mathrm{n}_1}\right)^2 + \left(\frac{\mathrm{n}_1 - \mathrm{n}_2}{\mathrm{n}_1 + \mathrm{n}_2}\right)^2 + 2\left(\frac{\mathrm{n}_0 - \mathrm{n}_1}{\mathrm{n}_0 + \mathrm{n}_1}\right)\left(\frac{\mathrm{n}_1 - \mathrm{n}_2}{\mathrm{n}_1 + \mathrm{n}_2}\right)\cos\left(\frac{4\pi}{\lambda}\mathrm{n}_1\mathrm{d}_1\right)}{1 + \left(\frac{\mathrm{n}_0 - \mathrm{n}_1}{\mathrm{n}_0 + \mathrm{n}_1}\right)^2\left(\frac{\mathrm{n}_1 - \mathrm{n}_2}{\mathrm{n}_1 + \mathrm{n}_2}\right)^2 + 2\left(\frac{\mathrm{n}_0 - \mathrm{n}_1}{\mathrm{n}_0 + \mathrm{n}_1}\right)\left(\frac{\mathrm{n}_1 - \mathrm{n}_2}{\mathrm{n}_1 + \mathrm{n}_2}\right)\cos\left(\frac{4\pi}{\lambda}\mathrm{n}_1\mathrm{d}_1\right)} \tag{11}$$

Using the assumption that the medium is air ($\mathrm{n}_0 = 1$), Eqn 11 can be written as:

$$\mathbf{R} = \frac{(1 + \mathrm{n}_1^2)(\mathrm{n}_1^2 + \mathrm{n}_2^2) - 4\mathrm{n}_1^2\mathrm{n}_2 + (1 - \mathrm{n}_1^2)(\mathrm{n}_1^2 - \mathrm{n}_2^2)\cos\left(\frac{4\pi}{\lambda}\mathrm{n}_1\mathrm{d}_1\right)}{(1 + \mathrm{n}_1^2)(\mathrm{n}_1^2 + \mathrm{n}_2^2) + 4\mathrm{n}_1^2\mathrm{n}_2 + (1 - \mathrm{n}_1^2)(\mathrm{n}_1^2 - \mathrm{n}_2^2)\cos\left(\frac{4\pi}{\lambda}\mathrm{n}_1\mathrm{d}_1\right)} \tag{12}$$

Equation 12 can be used to calculate the reflectance of a single thin film if the refractive index of the thin film (n_1), substrate (n_2), the thin film thickness (d_1) and wavelength is known. However, in dispersive materials the refractive index of the thin film layer and the substrate vary as a function of wavelength $[n_1 = nf_\lambda\ ;\ n_2 = ns_\lambda]$ due to the fact that that the speed of light through a material is dependent on the frequency of the light, thus the correct refractive indices must be used calculating the reflectance at a particular wavelength.

Equation 12 is not trivial to solve for the refractive index of the thin film as a function of measured reflectance at each wavelength. However, due to the fact that the cosine function is a periodic function the properties of this periodicity can be exploited. Due to the periodicity of the cosine function the reflectance of the thin film will increase and decrease in regular intervals. If the thickness of the thin film increases the reflectance will increase due to the thin film refractive index being greater than that of the substrate $(n_1 > n_2)$ or decrease when substrate refractive index is less than that of the thin film $(n_2 > n_1)$ until it reaches the first extrema (maximum and minimum respectively).

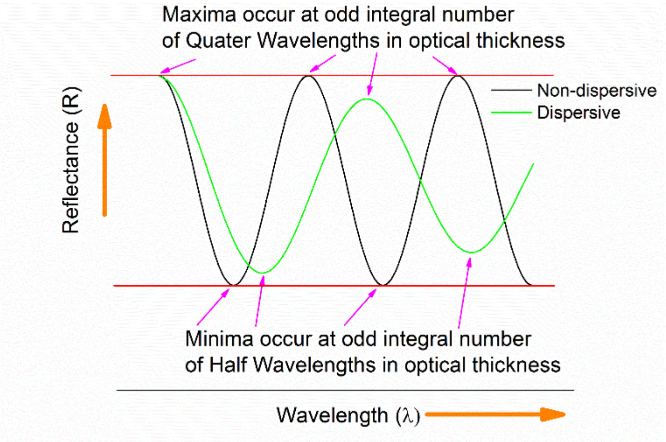

Figure S3: Reflectance maxima and minima in non-dispersive and dispersive material.

The reflectance maximum occurs when the thickness of the thin film corresponds to a quarter-wave optical thickness (QWOT) and has an order of 1 (m = 1) while the reflectance minimum occurs when the thickness of the thin film corresponds to a half-wave optical thickness (HWOT) which is equivalent to the reflectance of the uncoated substrate and has an order of 2 (m = 2). As the thickness of the thin film gets larger, reflectance will continue to increase and decrease in the same manner and this is shown in Fig. S3 above. If the thin film material is non-dispersive the reflectance maxima and minima would occur at the same values as shown in Fig. S3; however, if the thin film material was dispersive, the reflectance maxima and minima decrease in reflectance at longer wavelengths. This is due to the fact that the refractive index of the thin film and substrate decreases as the frequency of light decreases with increasing wavelength.

At each consecutive maxima the next higher odd order (3, 5, 7 etc.) occurs and at each consecutive minima the next higher even order (4, 6, 8 etc.) occurs which is the reflectance of the uncoated substrate. At the reflectance maxima $\cos\left(\frac{4\pi}{\lambda}n_1 d_1\right) = -1$, thus Eqn 12 for reflectance can be written as:

$$\mathbf{R} = \frac{(1+n_1^2)(n_1^2+n_2^2) - 4n_1^2 n_2 - (1-n_1^2)(n_1^2-n_2^2)}{(1+n_1^2)(n_1^2+n_2^2) + 4n_1^2 n_2 - (1-n_1^2)(n_1^2-n_2^2)} \tag{13}$$

Assuming that the thin film material is dispersive and by simplifying the above equation the reflectance can be reduced to,

$$\mathbf{Rf_\lambda} = \frac{\left(nf_\lambda^{\ 2} - ns_\lambda\right)^2}{\left(nf_\lambda^{\ 2} + ns_\lambda\right)^2} \tag{14}$$

where,

- nf_λ = Effective refractive index of the thin film at wavelength λ.
- ns_λ = Refractive index of the thin film at wavelength λ.
- $\mathbf{Rf_\lambda}$ = Maximum reflectance when order is odd of the thin film at wavelength λ.

Thus the refractive index of thin film at the reflectance maxima can be calculated using the formula:

$$nf_\lambda = ns_\lambda \left(\frac{1+\sqrt{\mathbf{Rf_\lambda}}}{1-\sqrt{\mathbf{Rf_\lambda}}}\right)^{0.5} \tag{15}$$

At the reflectance minima $\cos\left(\frac{4\pi}{\lambda}n_1 d_1\right) = +1$ and the equation for reflectance reduces to one where there is no nf_λ term thus the refractive index of the thin film cannot be calculated using reflectance minima. At the QWOT which is referred to as the first order (m = 1) the phase thickness ($2\delta_1$) is π radians thus by equating the phase thickness equal to π the thin film thickness (d) can be calculated:

$$\pi = \frac{4\pi}{\lambda_1} n_1 d \qquad \Rightarrow \qquad d = \frac{\lambda_1}{4n_1}$$

At each consecutive higher order the phase thickness increase by π radians, thus for second order the phase thickness is $2\pi = \frac{4\pi}{\lambda_2} n_2 d$ and for third order the phase thickness is $3\pi = \frac{4\pi}{\lambda_3} n_3 d$. Therefore at order *m* the phase thickness is $m\pi = \frac{4\pi}{\lambda_m} n_m d$, where λ_m and n_m are the wavelength and refractive index respectively of a specific m^{th} order thus, the thickness of the thin film can be calculated using the equation:

$$m\pi = \frac{4\pi}{\lambda_m} n_m d \qquad \Rightarrow \qquad d = \frac{m\lambda_m}{4n_m} \tag{16}$$

The value of n_m is calculated using Eqn 15 which is the effective refractive index of the thin film at the reflectance maxima which occur at consecutive odd orders. The refractive index of even orders can be calculated using Eqn 16 above using the thin film thickness (d) of the lowest odd order maximum. The order of maxima and minima increases from longer wavelengths to the shorter wavelengths due to the fact that the first minimum (m = 2) occurs at longer wavelengths.

Error Analysis for Reflectance: Refractive Index and Optical Thickness

The error in the calculated effective refractive indices (Δn_m) and the error in the calculated thin film thicknesses (Δd) at the odd orders can be calculated using the standard deviation of the changes in the effective refractive indices and thin film thicknesses respectively. Equations 15 and 16 depend on two measured quantities respectively. Thus, one can write Eqns 15 and 16 as a function that is dependent on two quantities, which for simplicity will be denoted as x and y, i.e. $f = f(x, y)$. Using the chain rule the change in the function (f) is simply given by:

$$\Delta f = \frac{\partial f}{\partial x}\Delta x + \frac{\partial f}{\partial y}\Delta y \tag{17}$$

Thus, the standard deviation of the function is given by the expression:

$$\Delta f^2 = \left\langle \left[\frac{\partial f}{\partial x}\Delta x + \frac{\partial f}{\partial y}\Delta y\right]^2 \right\rangle$$

$$\Rightarrow \Delta f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 \Delta x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \Delta y^2} \tag{18}$$

Thus, by applying Eqn 18 to Eqn 15 and 16 the error in the effective refractive index and thin film thickness are given by the following expressions:

$$\Delta \mathrm{n_m} = \sqrt{\left(\frac{1+\sqrt{\mathbf{Rf}_\lambda}}{1-\sqrt{\mathbf{Rf}_\lambda}}\right)(\Delta \mathrm{ns}_\lambda)^2 + \left(-\frac{\mathrm{ns}_\lambda^2}{4\left[\left(-1+\sqrt{\mathbf{Rf}_\lambda}\right)^3\left(1+\sqrt{\mathbf{Rf}_\lambda}\right)\mathbf{Rf}_\lambda\right]}\right)(\Delta \mathbf{Rf}_\lambda)^2} \quad (19)$$

$$\& \ \Delta d = \sqrt{\left(\frac{m^2}{16{n_m}^2}\right)(\Delta\lambda_m)^2 + \left(\frac{m^2{\lambda_m}^2}{16{n_m}^4}\right)(\Delta \mathrm{n_m})^2} \quad (20)$$

The error in the refractive indices of the substrate and the maximum reflectance is assumed to be to be 5 % and the error in the wavelength of light at which maximum reflectance occurs is the resolution of the spectrometer. Thus by using Eqns 19 and 20 the error in effective refractive indices and thin film thicknesses can be calculated.

Angle-resolved Reflectance Spectroscopy

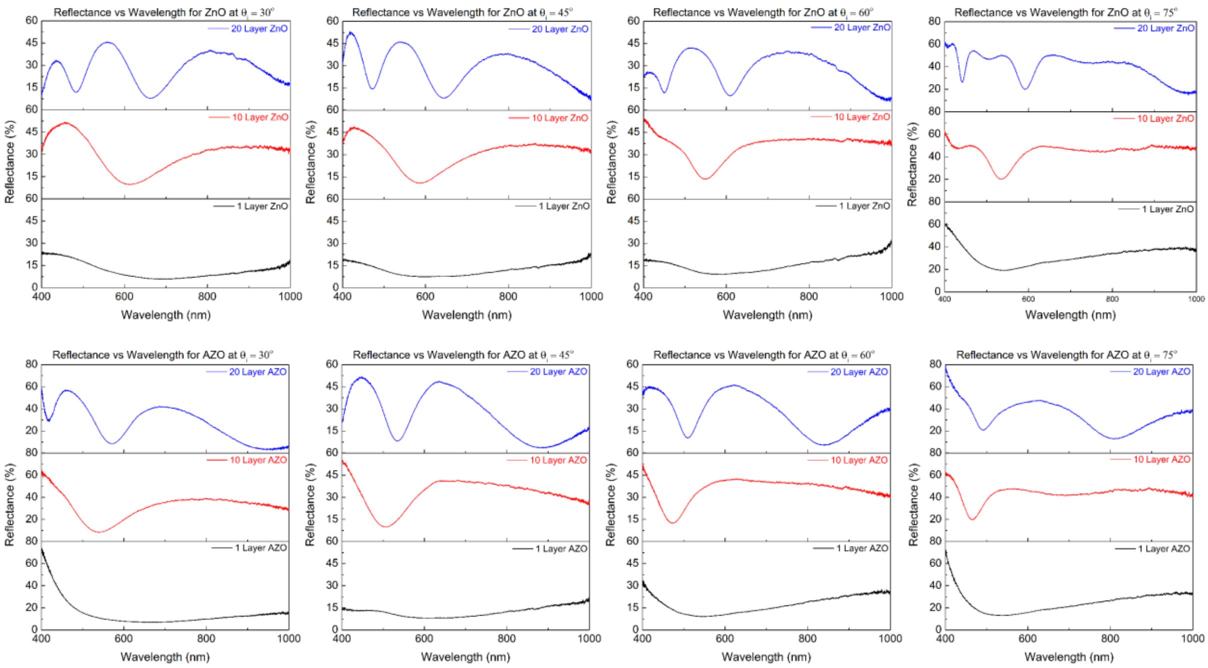

Figure S4: Reflectance spectra of 1, 10 and 20 layer ZnO and AZO films at various angles of incidence.