Modelling the spectral reflectances of miscellaneous ITO coatings by using only the Drude theory

N Wolf¹, D Gerstenlauer¹ and J Manara¹
¹Bavarian Center for Applied Energy Research (ZAE Bayern), Am Hubland, 97074 Wuerzburg, Germany

E-mail: nadine.wolf@zae.uni-wuerzburg.de

The spectral reflectances of miscellaneous TCO coatings were measured and analyzed with the Drude theory in the NIR region. The Drude model is a classical model and can be used to describe the dielectric behavior of metals and semiconductors quite well at wavelengths exceeding the plasma edge. Two types of sol-gel processed tin doped indium oxide (ITO) films deposited by dip-coating technique and a commercial sputtered ITO film were measured. The data for the optical and electrical parameters obtained from the modelling of the measured reflectance are in good agreement with those found in literature.

1. Introduction
Transparent conducting oxides (TCOs) combine physical material properties such as optical transparency and electrical conductivity, in order to provide spectrally-selective characteristics or transparent electrodes. Hence TCOs for example are used as coatings for energy-efficient windows [1], electrodes in flat-panel displays (LCD, OLED, PDP) [2], touch screens [3] and organic solar cells [4]. Tin doped indium oxide (ITO) is besides aluminum doped zinc oxide (AZO) and fluorine doped tin oxide (FTO) the most widely used material [5]. The optical and electrical properties of ITO can be understood in detail from the free-electron-theory [6]. Therefore ITO is the ideal material to verify if the measured normal hemispherical reflectance in the NIR region could be described by using only the Drude model which is used to describe free electrons in a material. In order to verify this, the normal hemispherical reflectance of two types of sol-gel processed and one commercial sputtered ITO were measured in the NIR region and the reflectances of these coatings were fitted with the Drude model as good as possible. Furthermore the parameters which were achieved through the fits are discussed.

2. Theoretical model
The complex dielectric function \( \varepsilon(\omega) \) describes the response of any material to electromagnetic waves and is related to the complex refractive index \( \tilde{n}(\omega) \) by the Maxwell-relation [7]

\[
\tilde{n}(\omega)^2 = \left( n(\omega) + i k(\omega) \right)^2 = \varepsilon(\omega) = \varepsilon'(\omega) + i \varepsilon''(\omega).
\] (1)

In this equation \( n(\omega) \) represents the real part of the refractive index, \( k(\omega) \) the imaginary part of the refractive index, \( \varepsilon'(\omega) \) the real part of the dielectric function and \( \varepsilon''(\omega) \) the imaginary part of the dielectric function. The normal reflectance \( R(\omega) \) at the interface air / material is given by the Fresnel equation [8]
\[ R(\omega) = \frac{(n(\omega) - 1)^2 + k(\omega)^2}{(n(\omega) + 1)^2 + k(\omega)^2} \]  

(2)

whereupon \( n(\omega) \) and \( k(\omega) \) could be described by \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) with

\[ n(\omega) = \sqrt{\frac{\varepsilon'(\omega) + \sqrt{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}}{2}}, \]

(3)

and

\[ k(\omega) = \sqrt{\frac{-\varepsilon'(\omega) + \sqrt{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}}{2}}, \]

(4)

To define the real and imaginary part of the dielectric function, the dielectric function itself has to be investigated more precisely. For the sake of clarity, in the following discussion only scalar fields are regarded and the frequency and time dependence are omitted.

For a more precisely investigation of the dielectric function a dielectric material under the influence of an external electric field \( E \) is regarded. This field separates the charge carriers in the material slightly which leads to a local electric dipole moment. The electric displacement field \( D \) is defined as

\[ D = \varepsilon_0 E + P_{\text{mac}}. \]

(5)

where \( \varepsilon_0 \) is the electric permittivity and \( P_{\text{mac}} \) the macroscopic polarization which is coupled to the electric field by [9]:

\[ P_{\text{mac}} = \varepsilon_0 \cdot \chi \cdot E, \]

(6)

\( \chi \) is the complex electrical susceptibility and considers all contributions to the polarization by \( \chi = \sum \chi_n \). Inserting equation (6) into equation (5) leads to

\[ D = \varepsilon_0 \cdot (1 + \sum \chi_n) \cdot E = \varepsilon_0 \cdot \varepsilon \cdot E, \]

(7)

where the (frequency-dependent) dielectric function can be identified. For a quantitative description of the properties of metals and doped semiconductors in the infrared spectral range, the dielectric function can be derived by [10]

\[ \varepsilon(\omega) = 1 + \varepsilon_{\text{VE}}(\omega) + \varepsilon_{\text{FC}}(\omega) + \varepsilon_{\text{PH}}(\omega). \]

(8)

\( \varepsilon_{\text{VE}}(\omega) \) represents the contribution of the valence electrons (which are considered to be bound in the observed spectral range), \( \varepsilon_{\text{FC}}(\omega) \) the contribution of the free charge carriers and \( \varepsilon_{\text{PH}}(\omega) \) the contribution of the polar optical phonons. Such a separation into different elementary excitations is possible if the individual susceptibilities correspond to resonances in well-separated frequency regions. In a frequency region which is far away from any resonance, every susceptibility is real and a constant [11]. \( \varepsilon_{\text{PH}}(\omega) \) is due to polar optical phonons, which couple to the applied electromagnetic field. The resonances occur in the far infrared [12] and therefore \( \varepsilon_{\text{PH}}(\omega) \) is negligible in this consideration. The interband transitions of valence electrons are represented in \( \varepsilon_{\text{VE}}(\omega) \) and the resonances are located at high energies in the ultraviolet. At wavelengths between 0.3 \( \mu \)m and 20 \( \mu \)m, which are well below the semiconductor band gap (ITO band gap lies at 3.6 eV which corresponds to a wavelength of 2.9·10^{-6} m) and the phonon resonance, equation (8) can be reduced to

\[ \varepsilon(\omega) = \varepsilon_\infty + \varepsilon_{\text{FC}}(\omega), \]

(9)

where \( \varepsilon_\infty \) represents a high-frequency dielectric constant [Jin 1988]. As in this paper n-doped semiconductors are investigated, \( \varepsilon_{\text{FC}}(\omega) \) originates from free electrons [12]. To describe the behavior
of the free electrons and therefore \( \chi_{\text{FC}}(\omega) \), the Drude model is used which is established for metals and is also applicable to our considerations. The optical properties of n-type semiconductors strongly depend on their electronic behavior as the plasma of nearly free electrons screens the incident electromagnetic wave via intraband transitions within the conduction band. This phenomenon is generally represented by the Drude model [13].

The Drude model was developed in 1900 by P. Drude, three years after J. J. Thompson discovered the electron. Drude was the first one who considered metals as a gas of electrons and applied the kinetic theory of gases to them to describe the electrical and thermal conduction [14]. This theory is based on several basic assumptions. First of all Drude postulated that some electrons in a metal can be considered to be free, i.e. they can be separated from their respective nuclei [15] and the free electron density \( N \) is equal to the density of metal atoms multiplied by their valency [16]. Furthermore any interactions of a given electron with other electrons or ions are neglected in the period between two collisions of this electron with an impenetrable ion core. A collision is considered to be an instantaneous event that abruptly changes the velocity and direction of any electron. Additionally these collisions are the only possibility for the electrons to achieve thermal equilibrium with the surrounding [14]. The central assumption of the Drude model is the existence of an average relaxation time \( \tau \) which represents the time between two collisions and is called collision time or mean free time [17]. Hence in the presence of an electric field, the free electrons get accelerated and then undergo collisions within the characteristic scattering time \( \tau \) [16].

Based on this theory the frequency-dependent electrical susceptibility \( \chi_{\text{FC}} \) can be described by

\[
\chi_{\text{FC}} = \frac{P_{\text{FC}}}{\varepsilon_0 \cdot E} = \frac{-N \cdot e \cdot x}{\varepsilon_0 \cdot E},
\]

where \( \varepsilon_0 \) represents the electric permittivity, and \( P_{\text{FC}} \) represents the electrical polarization, which is correlated to the above mentioned electron density \( N \), the electron charge \( e \) and the deflection \( x \) of the electrons [18]. Now the description of \( \chi_{\text{FC}} \) requires only the knowledge of the deflection \( x \) as the other quantities are constants (the electron charge \( e \) and electric permittivity \( \varepsilon_0 \)), induced from the outside (electric field \( E = E_0 e^{i \omega t} \)) or an intrinsic solid state quantity (electron density \( N \)).

The motion of the accelerated and slowed down electrons can be described by Newton’s law of motion [15]:

\[
m_{\text{eff}} \frac{d^2 x}{dt^2} + m_{\text{eff}} \frac{1}{\tau} \frac{dx}{dt} = -eE_0 e^{i \omega t},
\]

with the effective mass of the electrons \( m_{\text{eff}} \). The first summand on the left side in equation (11) is the acceleration term and the second term describes the damping with the scattering time \( \tau \). On the right hand side the propulsive force with the amplitude of the alternating electromagnetic field \( E_0 \) is given.

Equation (11) can be solved with the approach of a plane wave \( x = x_0 e^{i \omega t} \) which leads to this term for the deflection:

\[
x = \frac{e}{m_{\text{eff}}} \frac{1}{\omega \left( \omega + \frac{i}{\tau} \right)} \cdot E
\]

Inserting equation (12) and (10) in equation (9) finally yields to the dielectric function of metals and semiconductors:
\[ \varepsilon(\omega) = \varepsilon_{\infty} \left( 1 - \frac{N \cdot e^2}{\varepsilon_0 \varepsilon_{\infty} m_{\text{eff}}} \frac{1}{\omega (\omega + i \tau)} \right) = \varepsilon_{\infty} \left( 1 - \frac{\omega_p^2}{\omega (\omega + i \tau)} \right), \tag{13} \]

with the plasma frequency \( \omega_p = \frac{N \cdot e^2}{\varepsilon_0 \varepsilon_{\infty} m_{\text{eff}}} \). Accordingly the real part of the dielectric function is given by

\[ \varepsilon'(\omega) = \varepsilon_{\infty} \left( 1 - \frac{N \cdot e^2}{\omega^2 + \tau^{-2}} \cdot \varepsilon_0 \varepsilon_{\infty} m_{\text{eff}} \right), \tag{14} \]

and the imaginary part by

\[ \varepsilon''(\omega) = \frac{N \cdot e^2}{\omega \tau \cdot (\omega^2 + \tau^{-2}) \cdot \varepsilon_0 \varepsilon_{\infty} m_{\text{eff}}}. \tag{15} \]

The last two equations are also known as Drude equations [19]. Using the equations (14) and (15) together with (3) and (4), it is possible to determine the complex refractive index \( n^2 \). Finally the normal reflectance can be derived by equation (2). The measured normal reflectances can be fitted by varying the high-frequency dielectric constant \( \varepsilon_{\infty} \), the scattering time \( \tau \), the effective mass of the electrons \( m_{\text{eff}} \) and the electron density \( N \), whereby the fit was preformed and adjusted by using a least square procedure. By looking at equations (14) and (15) it can be seen, that the effective mass of the electrons \( m_{\text{eff}} \) and the electron density \( N \) are always linked in the ratio \( N/m_{\text{eff}} \) so that an infinite number of different \( N \) and \( m_{\text{eff}} \) can form the same ratio of \( N/m_{\text{eff}} \). Therefore only three parameters, that means the high-frequency dielectric constant \( \varepsilon_{\infty} \), the scattering time \( \tau \), and the ratio \( N/m_{\text{eff}} \) of the effective mass of the electrons \( m_{\text{eff}} \) and the electron density \( N \) are used for the fit.

### 3. Fits of the measured data

The measured normal hemispherical reflectance of a sputtered tin doped indium oxide (ITO) film and the measured normal hemispherical reflectance of two types of wet chemical processed ITO films deposited by dip coating have been fitted. The fits which describe best the measured data especially at the slope of the normal hemispherical reflectance are shown in Figure 1 till 3. The normal hemispherical reflectance \( R(\omega) \) has been measured in the wavelength range of 0.25 \( \mu \)m – 18 \( \mu \)m with the UV-VIS-NIR Spectrophotometer Lambda 950 and the FTIR spectrometer Bruker IFS 66v [20]. The specific electrical resistivity \( \rho \) was measured with a four point probe Nagy SD-600. With a Zeiss SMT Ultra Plus scanning electron microscope (SEM) the layer thicknesses were measured via SEM images of the breaking edges and the surface roughness of the layers were measured with a Veeco Dimension Icon atomic force microscope (AFM).

The sputtered ITO film has a thickness of about 310 nm and a surface roughness of about 0.5 nm. The first wet chemical processed ITO film was fabricated with a conventional sol. Within this so called high temperature method the sol is prepared with indium nitrate, stannic chloride acetylacetone and acetic acid dissolved in ethanol and acetone. The detailed preparation of the sol can be found in [21, 22]. This coating has a thickness of about 500 nm and a surface roughness of about 0.2 nm. The other wet chemical processed ITO film was fabricated with a nanoparticle suspension. This suspension consists of crystalline ITO nanoparticles which were redispersed in ethanol and ethylene glycol and stabilized with valeric acid and a organofunctionalized silane which acts as an organic-inorganic
cross-linking agent [23]. The coating is about 800 nm thick and has a surface roughness of 13 nm. The surface roughness of all layers are considerably smaller than the wavelength of the considered electromagnetic radiation and therefore these coatings show specular reflectance. The coatings were deposited on soda-lime glass and the thicknesses of all coatings are sufficient to avoid any contribution of the soda-lime glass to the measured reflectances, because the characteristic peaks of the soda-lime glass cannot be seen in the graphs.

The reflectance of the sputtered ITO coating is shown in Figure 1. This spectrum could be very well fitted using only the above described Drude model. In the calculations for the fit, the high-frequency dielectric constant was set to $\varepsilon_\infty = 4.4$, the scattering time to $\tau = 9.5$ fs and the ratio of the effective mass of the electrons and the electron density $\frac{m_{\text{eff}}}{N} = 35.7 \cdot 10^{26}$ m$^{-3}$/e$_m$.

![Figure 1](image)

**Figure 1.** Measured and fitted normal hemispherical reflectance $R(\lambda)$ of a sputtered ITO coating. The thickness of this coating is about 310 nm.

Figure 2 shows the measured normal hemispherical reflectance of the conventional sol ITO coating and a quite good fit of the measured data. The fit parameters were calculated to be $\varepsilon_\infty = 3.58$, $\tau = 3.5$ fs and $\frac{N}{m_{\text{eff}}} = 11.76 \cdot 10^{26}$ m$^{-3}$/e$_m$. This fit of the conventional sol ITO coating describes the slope between 1.1 µm and 2 µm and beyond 7 µm quite well, but between 2 µm and 7 µm the fit lies under the measured data. The fit could be improved by using the so called extended Drude model, which takes an energy and frequency dependent scattering time into account [24]. This scattering time is mainly due to the ionized impurity scattering (ISS), that means scattered by ionized dopant atoms [5, 25]. But in this paper only the plain Drude model is used.

The measured data and the fit of the nanoparticle suspension ITO coating is shown in Figure 3. The calculated values for this fit are $\varepsilon_\infty = 2.7$, $\tau = 2.4$ fs and $\frac{N}{m_{\text{eff}}} = 9.13 \cdot 10^{26}$ m$^{-3}$/e$_m$. Especially this fit of the nanoparticle suspension ITO coating could be improved besides the extended Drude model with the O’Leary-Johnson-Lim (OJL) model and the effective medium theory. The OJL model has been proposed to model the band gap of amorphous silicon [26].
Figure 2. Measured and fitted normal hemispherical reflectance $R(\lambda)$ of an ITO coating prepared with a conventional sol. The thickness of this coating is about 500 nm.

Figure 3. Measured and fitted normal hemispherical reflectance $R(\lambda)$ of an ITO coating prepared with a nanoparticle suspension. The thickness of this coating is about 800 nm.
It is used to describe the band gap transitions, that means the optical spectra in the region of the band gap ($\lambda < 500$ nm) [27]. This model is based on the assumption of parabolic conduction and valence bands with tail states exponentially decaying into the band gap [24]. The effective medium theory is used for heterogeneous materials that contains more than one phase (e.g. ITO and air) to account the porosity of a coating [24]. Coatings from crystalline nanoparticle suspensions consists of an agglomeration of these particles so that they are connected in a percolating network surrounded by air [5]. Therefore the porosity could be described by using an effective dielectric function. These values for all fits performed in this work are in a good agreement with those reported in the literature [5, 6, 19, 24, 28, 29, 30, 31]. The data for the optical and electrical properties given in literature exhibit large differences due to different production processes and therefore different composition of the samples [32], which corresponds to the results derived for the different ITO coatings shown above.

4. Discussion
The obtained values from these fits are consistent, that means the ratio of the effective mass of the electrons and the electron density, the scattering time and the dielectric constant of the three different coatings are related as expected. A summary of the values obtained by these fits and the expanded standard deviation of them is shown in Table 1. The parameters are not sensitive with the same magnitude in the model. The scattering time is less sensitive than the other two parameters. Assuming that all layers contain electrons which have approximately the same effective mass, the sputtered coating exhibits the highest charge carrier density whereas the charge carrier density of the nanoparticle suspension coating is lower than the charge carrier density of the conventional sol coating. The same is valid for the scattering time. This confirms that the porosity of the coatings increases and therefore the electrons in these coatings undergo more collisions.

The high-frequency dielectric constant $\varepsilon_\infty$ decreases from the sputtered coating to the conventional sol coating to the nanoparticle suspension coating. This is also explainable with the increasing porosity of the coatings.

| ITO coating          | $\varepsilon_\infty$ | $N m_{\text{eff}}/m_e$ [10$^{26}$ m$^{-3}$] | $\tau$ [fs] |
|----------------------|----------------------|-------------------------------------------|-------------|
| sputtered            | 4.4 ± 0.18           | 35.70 ± 1.66                              | 9.50 ± 1.17 |
| conventional sol     | 3.58 ± 0.04          | 11.76 ± 0.13                              | 3.50 ± 0.96 |
| nanoparticle suspension | 2.7 ± 0.11         | 9.13 ± 0.36                               | 2.40 ± 0.47 |

5. Conclusions
The Drude model was introduced in detail and the normal hemispherical reflectance of metals and doped semiconductors in the infrared spectral range was deduced by using this model. Based on these theoretical consideration it has been shown that it is possible to fit the measured normal hemispherical reflectance data of sputtered, conventional sol and nanoparticle suspension ITO coatings by using only the Drude equations. The values obtained through these fits are in good agreement with those reported in literature. Beyond that it was shown that these fits of the different coatings could be improved by extending the theory that is used for the fits. As it was mentioned, the extended Drude model taking an energy and frequency dependent scattering time into account, suffices for the improvement of the fit of the commercial sputtered ITO coating. Improving the fits of the two sol-gel ITO coatings requires,
besides the extended Drude model, also the OJL model which takes band gap transitions into account and the effective medium theory which regards the porosity of the coatings. Especially the fit of nanoparticle suspension ITO coating is in need of an effective medium theory.

If the theory of these fits is all-embracing so that the fits resemble the measured normal hemispherical reflectance very well, the values of these fits could be used to predict the behavior of these coatings without making other laborious measurements. This will be part of future activities.

6. References
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