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Approaches to calculate the dielectric function of ZnO around the band gap

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Abstract

Being one of the most sensitive methods for optical thin film metrology ellipsometry is widely used for the characterization of zinc oxide(ZnO), a key material for optoelectronics, photovoltaics, printable electronics and in a range of critical applications. The dielectric function of ZnO has a special feature around the band gap dominated by a relatively sharp absorption feature and an excitonic peak. In this work we summarize and compare direct (point-by-point) and parametric approaches for the description of the dielectric function. We also investigate how the choice of the wavelength range influences the result, the fit quality and the sensitivity. Results on ZnO layers prepared by sputtering are presented.

Keywords:
Spectroscopic Ellipsometry, ZnO, dielectric function, parametric dispersion model

1. Introduction

For a sensitive optical measurement of ZnO layers the dielectric function has to be known. If the sample is not single-crystalline, the dielectric function depends on the preparation conditions. For photon energies below the band gap, the refractive index is a smooth function of the photon energy,

consequently it can be modeled using simple dispersion equations like that of Cauchy [1]. This model is applied for the determination of the layer thickness. It has been shown by numerous authors, that the measurement of the optical properties of ZnO allows the indirect determination of its electrical properties [2, 3, 4] when the used spectral range includes the photon energies around the band gap. There are many approaches in the literature for the parameterization of the dielectric function of ZnO [5] in the gap region, including Adachi's model dielectric function [6], Holden model [7, 8], Elliott's formula [9], the Tauc-Lorentz (TL) model [10, 11] sometimes combined with a Drude oscillator for the IR part [3], model based on dispersion theories [12] or using a quadratic fit to the absorption edge [13]. There are other promising models like the Herzinger-Johs generalized critical point model [14] or the b-spline model by Johs and Hale [15] which can be useful to describe the dielectric function of ZnO.

In this study we compare a range of parametric models and discuss their capabilities in terms of fit quality, wavelength range and numerical values of the fitted parameters for sputtered ZnO.

2. Experimental details

ZnO layers with a thickness of ≈50 nm have been prepared using sputtering and annealed in forming gas at 400°C for 30 minutes. Si wafers were used as substrates with nominal thermal SiO_2 thicknesses of ≈10 nm. The nominal layer thickness of ZnO used in this investigation was 50 nm. The ellipsometric measurements have been performed using a Woollam M-2000DI rotating compensator spectroscopic ellipsometer. The evaluations have been made using both self-made and commercial software of the Woollam device.

3. Results and discussion

The ellipsometric spectra were measured in the photon energy range of 0.7-6.5 eV in 706 points at different angles of incidence (65°, 70° and 75°). The dielectric function of ZnO calculated by the b-spline model are plotted in Fig. 1. As revealed by Fig. 1, no absorption is expected below the band gap energy (≈3 eV), and there is a smooth dispersion for the real part of the dielectric function (ϵ_1), which allows the use of a Cauchy model in this wavelength range [16]. Ref. [16] is an example for the description of the dielectric function of ZnO with the Cauchy model below the band gap

energy range. We have described the ZnO layer with the Cauchy dispersion: $n = A_n + B_n/\lambda^2 + C_n/\lambda^4$ and $k = A_k exp(B_k[E - E_0])$, where n and k denote the refractive index and the extinction coefficient, respectively. During the fitting process, only the transparent region of the ZnO (from 0.7 eV to 2.5 eV) was used. For this reason, Cauchy parameters A_k and B_k didn't improve the fit quality. Therefore, the best fit model includes fitted parameters of A_n, B_n and C_n, as well as the thickness of the ZnO layer (50.7 nm) and its surface roughness layer (6.9 nm), as shown in Fig. 2. The region where Cauchy can be applied is also designated on Fig. 1.

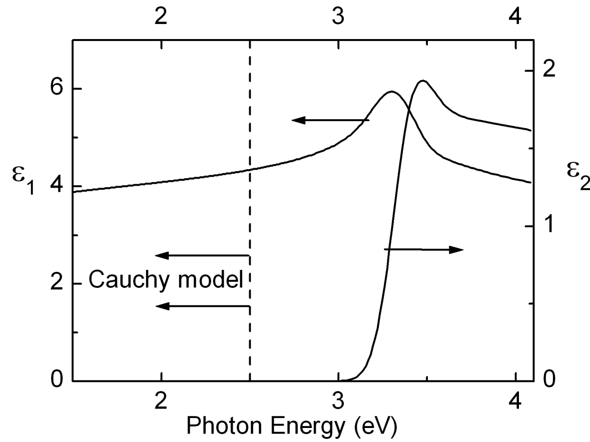

Figure 1: Typical spectra of the real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of ZnO (calculated from the b-spline model).

A dispersion model-independent determination of the dielectric function is the point-by-point (or direct inversion, [17]) method which utilizes the fact that the complex reflection coefficient measured by ellipsometry directly can be converted to both real and imaginary parts of the refractive index or dielectric function if the thickness of the layer is known. Fig. 3 shows that the spectra are strongly influenced by the layer thickness. However, the proper thickness can be determined by applying the constraint for the imaginary part of the dielectric function (ϵ_2) to gradually approach zero below the band gap energy [18]. In this approach a surface roughness layer was applyed with fixed value of thickness (determined by the Cauchy model with surface roughness). The dielectric functions of the ZnO were calculated by the point-by-point method using different thicknesses of the ZnO layer (46.7 nm, 47.7 nm, 50.7 nm and 53.7 nm). This is a reliable direct method, which

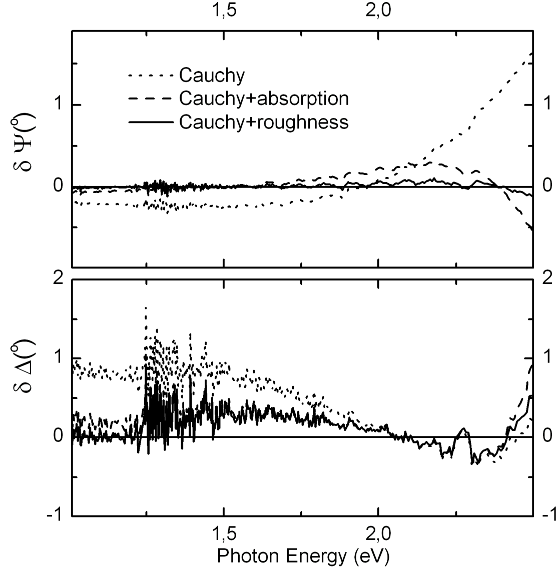

Figure 2: Differences between the measured and calculated spectra using a simple Cauchy model, a Cauchy model with absorption, and a Cauchy model without absorption but using a surface roughness in the wavelength range below the band gap. The angle of incidence was 65°.

doesn't require any assumption for the dispersion of the refractive index, and therefore can be used as a reference for the further parameterizations.

Note that the calculated dielectric function deviates significantly when changing the layer thickness, which is consistent with the results of Ref. [18] shown for polycrystalline silicon thin films (see Figs. 4 and 5 of Ref. [18]). This result points out the importance of using proper layer thicknesses according to the criterion of smooth transition of ϵ_2 at the gap, because the change of fit quality (MSE in Fig. 3) is large only towards the smaller thicknesses, as ϵ_2 would like to go negative, but is not allowed. The reason of the smaller sensitivity (in terms of MSE) is that in a point-by-point fit the spectral points are not coupled through a dispersion model, so the number of measured and fitted values are much closer than in case of a "coupled spectroscopic" fit (e.g. using the Cauchy model).

The TL model [19] is one of the frequently used models for ZnO [3, 4, 10] because the band edge can be described by a parabolic line shape and the excitonic absorption peak using several Lorentz oscillators. Even the effect

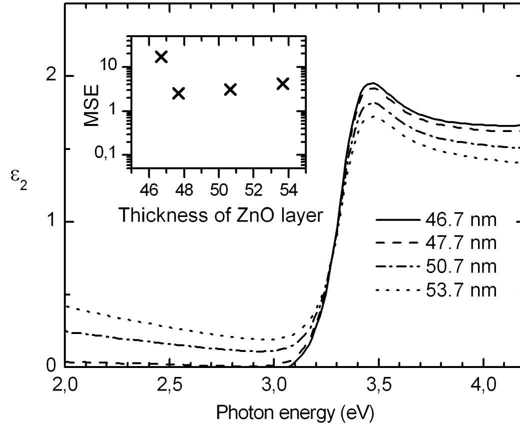

Figure 3: Imaginary part of the dielectric function determined using point-by-point inversion of the measured ellipsometric spectra with different thicknesses of the ZnO layer. The inserted graph shows the mean squared errors of point-by-point inversions.

of free electrons in the conduction band can be modeled by adding a Drude oscillator for the investigations in range of low photon energies. The latter term is not used in our model, because we limit the wavelengths to photon energies close to the band edge. In our model the TL dispersion formula was applied to describe the dielectric function of ZnO layer with 5 fit parameters: A (amplitude), C (broadening), E_0 (oscillator energy), E_g (band gap energy) and ϵ_{inf} (high frequency dielectric constant). The thicknesses of the ZnO layer and surface roughness layer were determined by the Cauchy model with surface roughness and were fixed at these values in the TL model. Different photon energy ranges were used for the fit. The lower limits were 0.7 eV, but the upper limits were changed between 2.6 eV and 4.1 eV with a step of 0.1 eV (Fig. 4 shows one of the fitted spectra).

Fig. 5 demonstrates that the fit result strongly depends on the photon energy range around the band gap energy used for fitting the spectra. A stable curve which remains the same when further increasing the photon energy range is reached at around 4 eV and deteriorates again for higher photon energies (close to 5 eV) that include further transitions. All fitted parameters but A are stabilized above the photon energy of 3.5 eV, in other words, their values don't change significantly when further increasing the upper limit of the photon energy range (Fig. 6). The parameter uncertainties reach acceptable limits also only in this range.

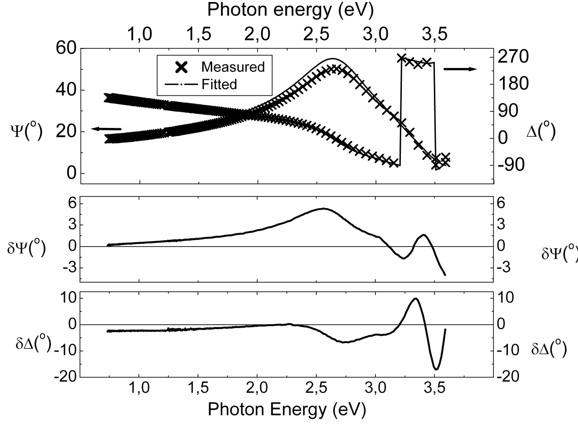

Figure 4: Measured and calculated spectra by applying Tauc-Lorentz formula in the photon energy range of 0.7-3.6 eV. $\delta\Psi$ and $\delta\Delta$ mean the differences between the measured and calculated spectra of Ψ and Δ respectively. The angle of incidence was $65°$.

The reason of the increasing deviations when decreasing the upper limit of the photon energy range used for the fit is that smaller and smaller part of the excitonic peak is involved in the fit range. Consequently, the sensitivity of all parameters that describe this peak (most importantly E_0 and C) decreases. One of our most important message is however not only the decrease in parameter sensitivity, but also to show that this effect seriously influences the line shape of the determined dielectric function, as shown in Fig. 5. Therefore, it is important to note that, when fitting ZnO thin films, not only the choice of the proper optical model (dispersion function) but also the proper photon energy range is crucial: for lower photon energies the excitonic peak is not included, for larger photon energies other transitions are included, which are not described by the single oscillator TL model. Of course, the sensitivity of correlating parameters can be increased when setting those (E_0 and C) parameters at fixed values for lower photon energy ranges. However, when the increased energy range reaches the oscillator, the parameters fixed at wrong values will significantly influence the determined dielectric function (as shown in Fig. 5).

In contrast to the TL model the Herzinger-Johs [14] dielectric functions parameterization uses Gaussian-broadened polynomials to describe the interband transition features. It is an empirical model that allows to add several oscillators which can be adapted to virtually any critical point line shapes. This feature is also a disadvantage, because it requires the oscillator parame-

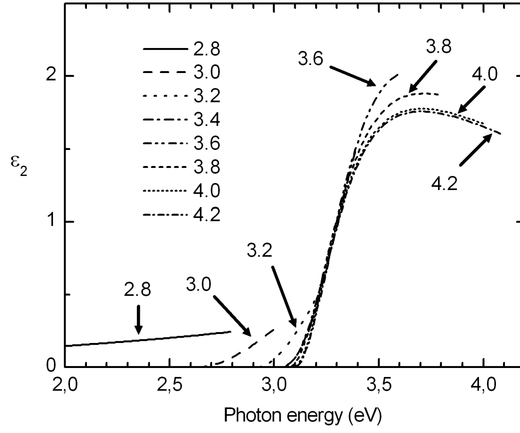

Figure 5: Imaginary part of the dielectric function determined by fitting the Tauc-Lorentz parametric model to the measured data using different wavelength ranges. The legend shows the upper limits of the range in eV.

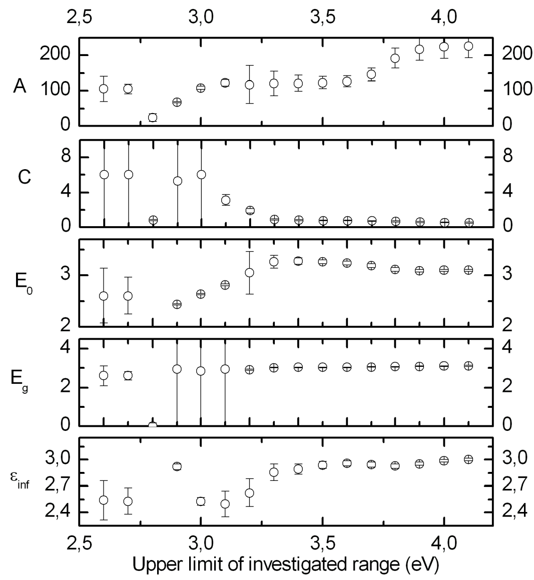

Figure 6: Fitted parameters of the Tauc-Lorentz model as a function of the upper limit of the investigated wavelength range. A, C, E_0, E_g, and ϵ_{inf} denote amplitude, broadening, oscillator energy, band gap energy and the shift for the Kramers-Kronig compensation, respectively.

ters to be chosen carefully, in order to keep the total number of fit parameter within a reasonable number.

The dielectric function spectra calculated by the Herzinger-Johs model were consistent for all upper limit values (Fig. 7). As initial set of oscillator parameters the "Psemi-M0" type was used with 6 fitting parameters: A (amplitude), Br (broadening), E_0 (oscillator energy), ϵ_{inf} (high frequency dielectric constant), PR and WR (polynomial control point parameters). Because the critical point features are described by connected polynomials, the model can describe any types of critical points. In that sense we considered the approach fully empirical, and didn't further analyze the fitted values in terms of critical point types. Not surprisingly, the parameter values get stabilized above a similar photon energy value (≈3.5 eV, Fig. 8) as in the case of the Tauc-Lorentz fit (Fig. 6), but for this model none of the parameters change any more above the upper limit value of 3.5 eV. Fig. 9 shows one of the fitted spectra in the photon energy range of 0.7-3.6 eV.

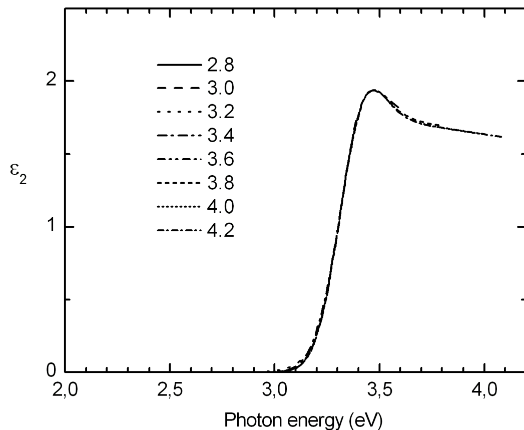

Figure 7: Imaginary part of the dielectric function determined by fitting the Herzinger-Johs parametric model to the measured data using different wavelength ranges. The legend shows the upper limits of the range in eV.

The results obtained using the different parameterizations are consistent in the band gap region, but the limitation of flexibility above the band gap leads to variations that will get worse as more photon energy range is utilized (Fig. 10). The peak position of the Tauc-Lorentz model is shifted, however the gap region is close to that of the other models. Note that the B-spline model [15] is a more robust version of the direct inversion, because the mea-

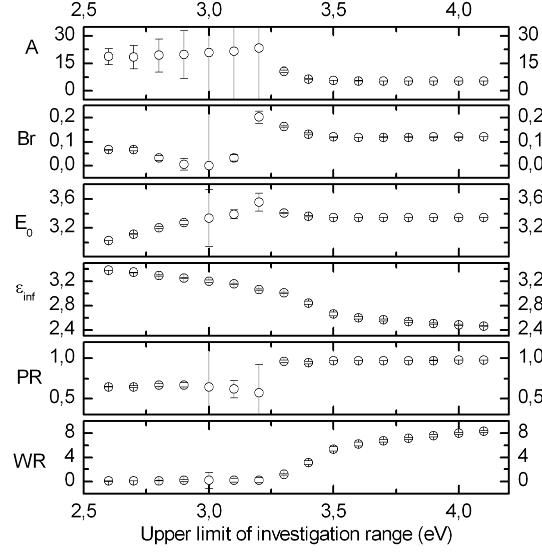

Figure 8: Fitted parameters of the Herzinger-Johs model as a function of the upper limit of the investigated wavelength range. A, Br, E_0, and ϵ_{inf} denote amplitude, broadening, oscillator energy, and shift for the Kramers-Kronig compensation. PR and WR are polynomial control point parameters.

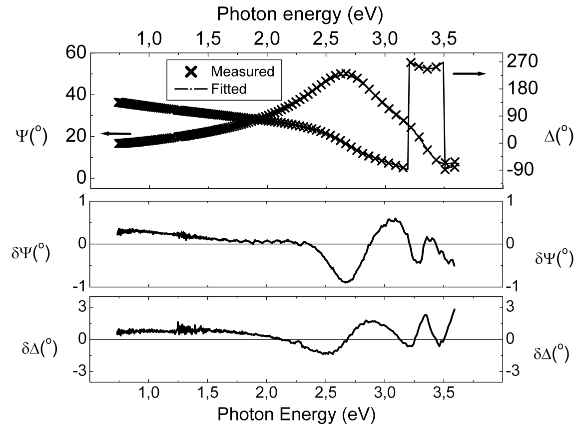

Figure 9: Measured and calculated spectra by applying Herzinger-Johs formula in the photon energy range of 0.7-3.6 eV. $\delta\Psi$ and $\delta\Delta$ mean the differences between the measured and calculated spectra of Ψ Δ respectively. The angle of incidence was 65°.

sured data are not independently fitted in each spectral point, but several points within a range (usually 0.1-0.3 eV, in this case 0.12 eV) are connected and fitted by a B-spline with several polynomial parameters. This model uses a largely reduced number of fit parameters but still allows a quasi dispersion model-independent fit. In most cases even the layer thickness can be fitted with high reliability. In our case, the thicknesses of both the ZnO and roughness layers were fixed to values determined from the Cauchy model. In the B-spline model, no limitation is set for ϵ_2. The resolution was 0.12 eV, which means that for example in case of the photon energy range of 0.7-6.5 eV the number of control points was 24 and the number of free parameters was 48.

In case of the point-by-point model two parameters (ϵ_1 and ϵ_2) are fitted on 6 measured values ([Ψ,Δ] pairs at 3 angles of incidence) at each wavelength independently. For the B-spline model, short wavelength regions are connected through polynomials, which means that the number of fitted parameters and measured values are still close. In case of the other two parametric dispersion models a few (5 and 6) parameters are fitted on a large (>1000) number of measured data, for which a simple dispersion is assumed over a large photon energy range. This explains why the MSE values are much larger for the latter models.

Figure 11 shows the mean square error (Er) values of the different models as a function of the upper limit of photon energy range used in the fit. The Er was defined by:

$$Er = \sqrt{\frac{1}{2N}\sum_{i=1}^{N}\left(\left(\Psi_i^{meas} - \Psi_i^{cacl}\right)^2 + \left(\Delta_i^{meas} - \Delta_i^{cacl}\right)^2\right)}, \qquad (1)$$

where Ψ and Δ are the ellipsometric angles and N is the number of independently measured values corresponding to different wavelengths. *meas* and *calc* refer to measured and calculated values, respectively. The point-by-point and the B-spline models have the lowest values as expected, because of the larger number of fitted parameters. The Herzinger-Johs and Tauc-Lorentz models have nearly the same number of fit parameters with significantly lower Er values of the Herzinger-Johs model. In spite of the different Er values, the determined dielectric functions are very similar for the Herzinger-Johs, B-spline and point-by-point models, showing that the difference in Er doesn't necessarily mean a wrong dielectric function, it is rather related to the reliability of the result.

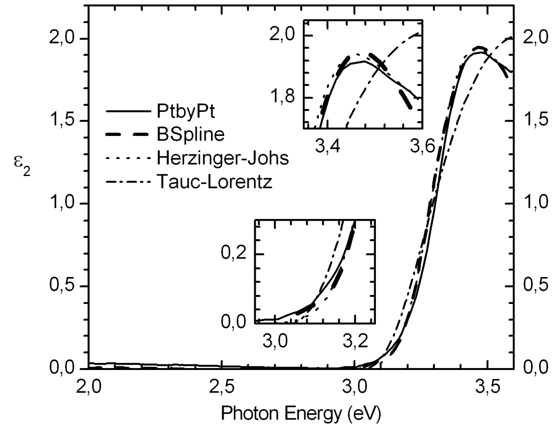

Figure 10: Summary of the imaginary part of the dielectric function fitted using different parameterizations with 3.6 eV upper limit of wavelength range.

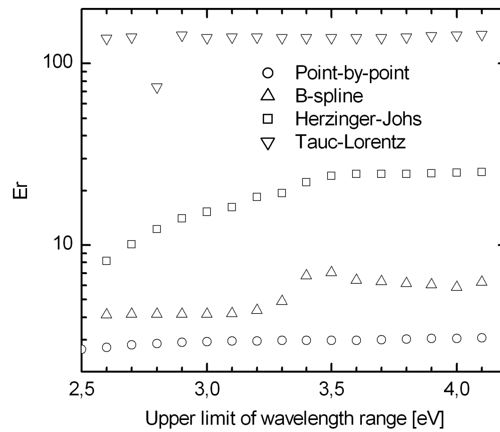

Figure 11: Mean squared errors of fits using different models as a function of the upper limit of the photon energy range used in the fit.

Conclusions

Different parameterizations of the dielectric function of ZnO have been compared around the band gap. The Cauchy model can be used in the below band gap photon energy range to calculate the surface roughness and the layer thickness, which can be used as fixed parameters in the parametric models, especially in the direct inversion, which doesn't allow the use of more

than two fit parameters (ϵ_1 and ϵ_2 at each wavelength). Direct inversion and B-spline models were found to be safe choices when using surface roughness values determined by the Cauchy fit at lower photon energies. The thickness of the layer can be found by applying the restriction for ϵ_2 to approach zero below the band gap. It has been shown that the used wavelength range has a major influence on the values of the fitted parameters. Above approximately 3.5 eV the values were consistent. In addition to the point-by-point and the B-spline models the Herzinger-Johs model also provided the same dielectric function values, whereas for the Tauc-Lorentz model a discrepancy was found around the exciton peak energy of $\approx$3.4 eV. The advantage of the Tauc-Lorentz model is that it immediately provides the band gap values, while in case of the other models further analysis is required for its determination.

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