Exemplary analysis of a multilayer system on glass: interplay between optical characterization and mass spectrometry

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An exemplary analysis of a transparent multilayer system on glass is performed. Optical measurements and simulations reveal the number of layers and the optical constants as well as the thickness of each layer. The results are confirmed by secondary neutral mass spectrometry which provides information on the layer composition and the substrate as well as the number and thicknesses of the layers. The optical constants of the layers show significantly different dispersion relations.

1 Introduction

In many research areas, sample analysis focusses on characterization of a single layer deposited on a well-known substrate. Extensive investigation with different characterization techniques is performed to optimize the optical, microstructural, and electrical properties of this layer for the application of interest by varying the deposition parameters [1]. However, in a complex multilayer system it is not only the performance of a single layer but also the interplay of all involved layers. For thin film solar cells, for example, it is essential to understand the influence of each layer on the overall performance of the entire module, e.g. sodium diffusion from the glass into the $Cu(In,Ga)Se_2$ absorber improves solar cell efficiency [2].

The analysis of multilayer systems gains importance. The optical investigation of multiple thin films is frequently performed with ellipsometry [3], but it does not supply reliable results for transparent materials, e.g. glass substrates. Determination of absorption coefficients, α, smaller than 100 cm^{-1} is difficult with ellipsometry [4] therefore transmittance measurements have to be added [5]. To extract physical parameters from photometric or ellipsometric measurements, optical simulations are performed. This is a powerful and non-destructive tool for sample analysis. Another powerful but destructive way of layer characterization offers depth profiling using surface analytical methods like electron spectroscopy and mass spectrometry.

In this work, a transparent multilayer system on glass with an unknown number of layers and layer properties is analysed exemplarily using optical and surface analytical techniques. Optical simulations are performed to obtain the optical constants and the layer thicknesses. SNMS experiments provide information on the chemical composition of the layers.

2 Experimental details

Transmission spectra were recorded with an UV/Vis/NIR spectrophotometer (Perkin Elmer Lambda 1050) coupled to a 150 mm integrating sphere with tungsten halogen and deuterium lamps as light sources and photomultiplier (Hamamatsu R6872) and Peltier-cooled InGaAs photodiode for detection. Ellipsometric data were recorded with a spectral ellipsometer (Semilab GES5E) at an incidence angle of 60°. A xenon lamp (75 W) was used as light source and photomultiplier and InGaAs photodiode as detectors. Optical simulation was performed with the software package CODE [6].

Secondary neutral mass spectrometry (SNMS) is a well-suited method for the investigation of conductive or non-conductive thin films and thin film systems. The experiments were performed with the SPECS INA-3 system in the so-called High Frequency Mode (HFM) [7, 8]. A square-wave with an amplitude of 750 V and a frequency of 600 kHz was applied to the sample. To reduce charging effects the ratio between negative and positive phase was 0.4. The surface was sputterremoved by Ar^+ ions of 0.8 keV with a material depending rate of about 0.2 nm/sec.

X-ray diffraction (XRD) measurements were performed in Bragg-Brentano focusing geometry using copper K_α radiation from an AXS D8 Advance diffractometer (Bruker) operating at 40 kV and 40 mA. Cross-sectional profiles were taken with an Ambios Technology Profilometer XP-2.

3 Results and discussion

3.1 Optical properties and optical simulation

The first, but very important step in multi-layer analysis is to obtain precise information on the optical properties of the substrate. For this, the sample was mechanically polished to remove the coating. The thickness of the glass substrate is 3.2 mm, which is a typical thickness for photovoltaic glass [9]. Subsequently, the optical transmission and reflection spectra of the substrate are recorded (Figure 1a). The broad absorption in the near infrared spectral range (600 to 1500 nm) and the onset of the ultraviolet absorption at 330 nm are typical for a standard float glass. The glass spectra are simulated using Kim oscillators [10] (Figure 1b); the obtained optical constants, namely the refractive index, n, and the extinction coefficient, k, are in good agreement to literature values [5]. The refractive index, n, at 633 nm is approx. 1.5 and increases in the ultraviolet spectral range; the extinction coefficient, k, features the characteristic iron absorption bands at 380 nm and the broad band peaking at 1080 nm due to ferric iron (Fe_2O_3) and ferrous iron (FeO) [11], respectively.

Figure 2a shows the experimental optical spectra for the coated glass. The oscillations clearly indicate the existence of a thin film on the glass. For the subsequent optical simulation, the optical constants for the substrate are set to the values obtained from above and kept constant during the fitting procedure. A Kim oscillator is used for the ultraviolet absorption, while the Drude model [12, 13] is used to describe the behaviour in the infrared spectral range which is mainly induced by free carrier absorption. In addition, it is assumed that the oscillations are caused by a single layer only. The result is depicted in Figure 2a, red curves. In the ultraviolet and near infrared spectral range, the simulation is in good agreement with the experimental data. Between 900 and 1500 nm, however, there is a discrepancy which indicates that assuming a single layer only does not allow for a good fit in the near infrared spectral range. The simulation results in a layer thickness of approx. 1020 nm (Figure 2a, inset); the corresponding optical constants are plotted in Figure 2b. The refractive index, n, shows a typical transparent conducting oxide (TCO)-like

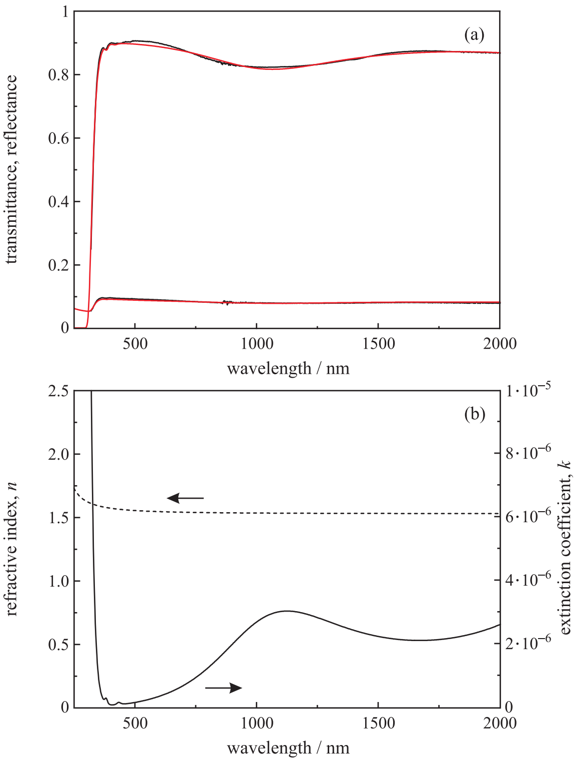

Figure 1: Glass substrate: (a) Experimental (black) and simulated (red) optical spectra, (b) simulated refractive index (dashed) and extinction coefficient (solid).

dispersion (see Figure 2b, dotted curve) [14]. The extinction coefficient, k, shows an increase in the ultraviolet spectral range due to band gap absorption, and in the near infrared spectral range due to free carrier absorption (see Figure 2b, solid curve).

To obtain a better fit a second layer was added to the simulation (Figure 3a, inset). The simulated optical spectra (Figure 3a, red curves) show a good agreement between simulation and experiment now. The layer thicknesses amount to approx. 930 nm for the top and 100 nm for an additional bottom layer. The total thickness of the two layers agrees with the single layer thickness from above. The simulated optical constants are depicted in Figure 3b. The optical constants of the top layer (bluish curves) show only slight deviations from the single layer simulation (Figure 2b). The refractive index, n, of the additional bottom layer (see Figure 3b, dashed greenish curve) shows little dispersion and very low conductivity due to a low extinction coefficient in the near infrared spectral range. This layer seems to be a buffer layer to reduce diffusion from glass components in the TCO layer.

Ellipsometric data of the coated sample are shown in Figure 4 (black curves). The bad signal-to-noise ratio for wavelengths higher than 1200 nm is caused by low reflectance of the sample. For the

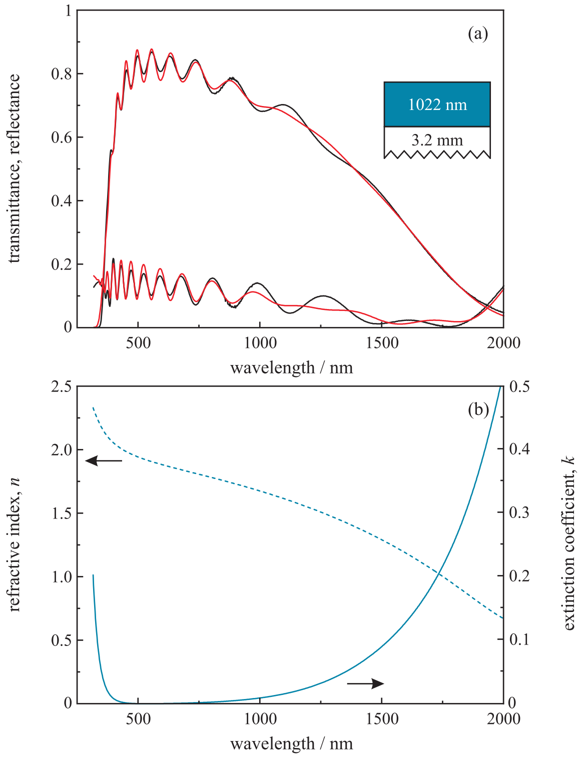

Figure 2: Coated glass: (a) Experimental (black) and simulated (red) optical spectra, (b) simulated refractive index (dashed) and extinction coefficient (solid). The simulations are performed for a single layer system on glass. The inset shows the layer stack used for the simulation.

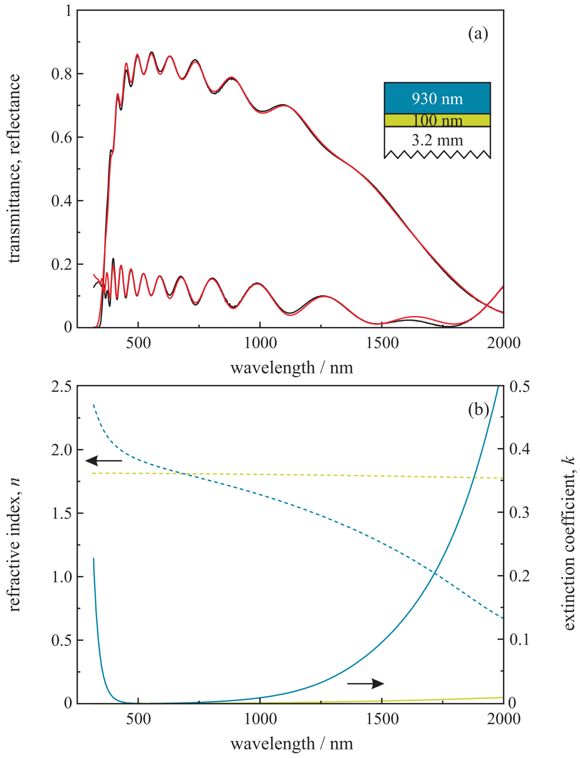

Figure 3: Coated glass: (a) Experimental (black) and simulated (red) optical spectra, (b) simulated refractive index (dashed) and extinction coefficient (solid). The simulations are performed for a double-layer system on glass. The inset shows the layer stack used for the simulation.

simulation, the optical constants from Figures 2b and 3b are used. Again, the fit result assuming a single layer on the glass substrate (Figure 4a) shows significant deviations in the near infrared spectral range. Simulations assuming a double-layer system, however, result in good agreement to the experimental data (Figure 4b). The results of the different simulation steps are summarized in Table 1.

3.2 Depth profile analysis using SNMS

The results of the optical investigations are confirmed by mass spectrometric depth profile analysis. SNMS experiments (Figure 5) provide the chemical composition, information on the number of layers and the layer thicknesses.

The analysis yields two layers on a float glass substrate which is mainly comprised of sodium, magnesium, silicon, and oxygen. Coming from the glass side, the first layer (buffer layer) is characterized by a high aluminium content, while the oxygen and silicon signals show the same intensities as in the glass. In addition, the first layer shows decreasing magnesium and sodium signals. Magnesium and sodium ions in the glass probably diffuse during ion bombardment from the glass into the adjacent layer induced by charging effects.

The top layer is likely to be an aluminium-doped zinc oxide (AZO) film for oxygen, zinc, and aluminium being the most pronounced signals, but also some impurities like sodium from the glass can be detected. X-ray diffraction shows a single reflection at approx. $2\theta = 34°$ (data not shown) confirming the AZO composition of the film [15]. The thickness of the top layer is significantly higher than that of the buffer layer.

The SNMS sputter crater depth, analysed by profilometry, has a depth of 1070 nm in the centre. This matches very well the simulated total layer thickness of 1030 nm for both layers. Note, that in the SNMS experiments also a few nanometers of the glass substrate were removed.

4 Conclusion

A multilayer system with a transparent substrate was characterized by optical spectroscopy and subsequent optical simulation. The investigated system consists of a 3.2 mm thick float glass substrate

Table 1: Layer thicknesses and optical constants at 633 and 1000 nm, obtained by optical simulations.

simulation	layer	thickness, d in nm	refractive index, n at 633 nm	refractive index, n at 1000 nm	extinction coefficient, k at 633 nm	extinction coefficient, k at 1000 nm
substrate	glass	3.2 mm	1.54	1.54	$5.0 \cdot 10^{-7}$	$27.0 \cdot 10^{-7}$
single layer system	layer	1022	1.87	1.68	$1.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-3}$
	glass	–	–	–	–	–
double layer system	bottom layer	930	1.84	1.65	$1.1 \cdot 10^{-3}$	$9.6 \cdot 10^{-3}$
	top layer	100	1.81	1.80	$0.3 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$
	glass	–	–	–	–	–

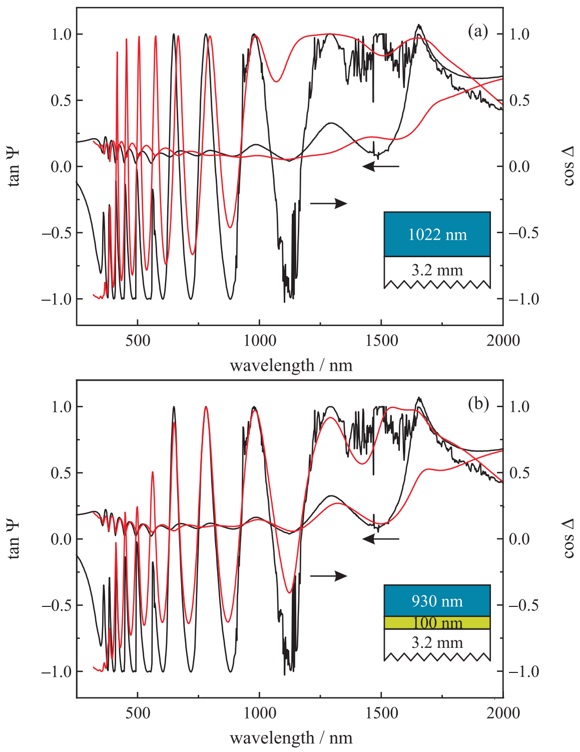

Figure 4: Coated glass: Experimental (black) and simulated (red) ellipsometric spectra for (a) the single layer and (b) the double-layer system. For the simulation, the optical constants from Figures 2b and 3b were used.

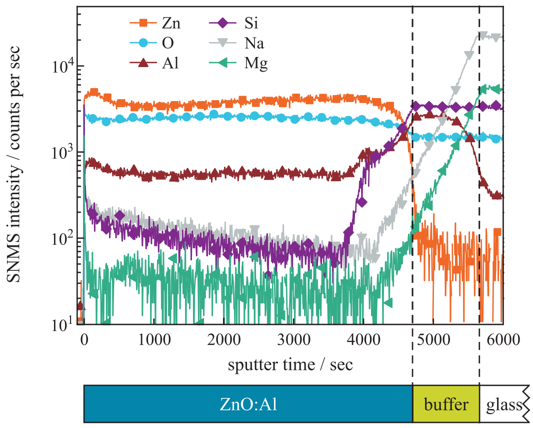

Figure 5: SNMS depth profile of the TCO coated sample.

coated with a 930 nm thick TCO layer and a 100 nm buffer layer in-between. These results are confirmed by SNMS and profilometry. In addition, SNMS reveals ZnO:Al as the composition of the TCO-layer and SiO_x:Al of the buffer layer.

To conclude, optical spectroscopy combined with optical simulation is often used to analyse the optical properties of single or double coated glass substrates. For complicated layer stacks, however, additional information on the layer thicknesses and the chemical composition is helpful. This information can be obtained by surface analytical methods. The combination of both methods combined with optical simulation provides a powerful tool for process and quality control of glasses with functionalized coatings.

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References

[1] M. Berginski, J. Hüpkes, W. Reetz, B. Rech, W. Wuttig, Thin Solid Films 516, 5836 (2008)

[2] J.-H. Yoon, T.-Y. Seong, J.-h. Jeong, Prog. Photovolt: Res. Appl. 21, 58 (2013)

[3] M. Ahles, T. Ruhl, G. P. Hellmann, H. Winkler, R. Schmechel, H. von Seggern, Opt. Comm. 246, 1 (2005)

[4] H. Fujiwara, Spectroscopic Ellipsometry: Principles and Applications, John Wiley & Sons Inc, 2007

[5] R. A. Synowicki, B. D. Johs, A. C. Martin, Thin Solid Films 519, 2907 (2011)

[6] M. Theiss, Hard- and Software for Optical Spectroscopy, Dr. Bernhard-Klein-Str. 110, 52078 Aachen, Germany, http://www.mtheiss.com

[7] H. Oechsner, K.-H. Müller, "Process and device for the analysis of superficial and/or deep profiles", International Patent Application WO 92/13268 (1992)

[8] H. Bubert, H. Jenett, "Surface and Thin Film Analysis", Wiley-VCH, 2003

[9] J. E. Webb, D. I. Wilcox, K. L. Wasson, S. T. Gulati, 24th European Photovoltaic Solar Energy Conference, Hamburg, Germany, September 21-25, 2009, 3253

[10] C. C. Kim, J. W. Garland, H. Abad, P. M. Raccah, Phys. Rev. B 45, 11749 (1992)

[11] J. K. Goodyear, V.L. Lindberg, Sol. Energ. Mater. 3, 57 (1980)

[12] P. Drude, Ann. Phys. 306, 566 (1900)

[13] P. Drude, Ann. Phys. 308, 369 (1900)

[14] Z. H. Qiao, C. Agashe, D. Mergel, Thin Solid Films 496, 520 (2006)

[15] Z. Zhang, C. Bao, W. Yao, S. Ma, L. Zhang, S. Hou, Superlattice Microst. 49, 644 (2011)