Reflectance spectroscopy as a method for the contact-less determination of the quality of thin coatings on glass

A. Kraft, M. Rottmann
Gesimat GmbH, Berlin, Germany

Abstract

A fast, non-contact measuring technique for the determination of the quality of several functional coatings on glass is presented. The measuring technique is based on simple reflection spectroscopy in the UV, visible and/or infrared spectral range. It can replace established methods such as four-point probe, eddy current or other techniques. The use of state-of-the-art spectroscopic equipment such as fibre optics and detector arrays allows to construct a cost efficient device for fast, non-contacting, non-destructive surface scanning evaluation of large area glass products coated with e.g. TCO, low-e, photovoltaic, photocatalytic, mirror or electrochromic coatings. This measurement method can be used either as a quality control tool or in-situ in a coating line for process control of thin film deposition.

Keywords: thin films, quality control, reflectance spectroscopy

1. Introduction

Thin solid films are applied to glass surfaces to adapt the properties of glass to a multitude of different uses.

Transparent conducting oxide (TCO) films such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO) or ZnO:Al are used to provide electrical conducting surfaces or low-e properties. More advanced low-e coatings on glass generally consist of a stack of different layers containing very thin silver films as the essential material. They are used in modern architectural glazing for controlling the U value of windows. Thicker silver films on glass are used for mirror applications. Thin semiconductor films such as CdTe or $CuInS_2$ are produced on glass for photovoltaic applications. TiO_2 thin films are used either for photocatalytic or also for photovoltaic applications. Diamond-like carbon films can be used for the scratch protection of glass surfaces. Electrochromic films such as tungsten oxide or nickel oxide are part of electrochromic film stacks which provide switchable optical properties.

Most of these thin film materials are electrical conducting, their conductivity varying to a great degree. Different conductivities are accompanied by differences in the properties of these films which can easily be measured by reflectance spectroscopy in the appropriate wavelength range.

2. Measuring method and evaluation

2.1 Reflectance spectroscopy

The spectroscopic measurement of the reflection of electromagnetic radiation from a surface is one of the most convenient techniques for the study of the surface properties and composition of materials. Modern equipment such as diode array spectrometers, light guide fibers etc. allow to construct lightweight, small, easy to handle and cost-effective analytical tools even for in situ analysis during thin film coating [1].

2.2 Plasmon oscillations

Electrical conductivity in materials is associated with moveable free charge carriers. The conductivity in general is proportional to both the number of free charge carriers (i.e. the charge carrier concentration N) and their mobility μ. Therefore, if N and μ are known the electrical conductivity can be calculated.

A contact-less determination of N and μ is possible by an optical excitation of the free charge carriers in an object which has to be studied. The collective oscillations of free charge carriers against lattice atoms are called plasmon oscillations. Depending on the charge carrier concentration of the material they are active in the UV, Visible, NIR or IR spectral range. This can be recognised in the reflection spectra as a plasma reflection edge, a steep rise in reflectivity starting from a minimum value. Figure 1 shows a typical reflection spectra in the range of the plasma reflection edge.

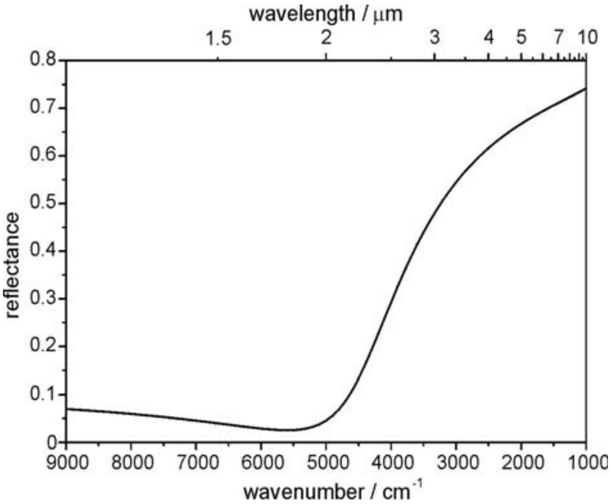

Fig. 1. Typical reflection spectrum of a material in the area of the plasma reflection edge

2.3 Mathematical modelling

The spectral position of the plasma reflection edge depends on the charge carrier concentration according to equation 1.

$$\omega_p = \sqrt{\frac{Ne^2}{m^* \varepsilon_\infty \varepsilon_0}} \qquad (1)$$

with ω_p the plasma frequency and m^* the free carrier effective mass.

The higher the charge carrier concentration the higher the plasma frequency. Therefore, plasmon oscillations for different materials are excited in different spectral regions. In many semiconductors the plasma reflection edge can be found in the far infrared. The plasma frequency of transparent conducting oxides lies in the near infrared. For most metals it is found in the UV.

The form or better the steepness of the rise of the reflectivity around the plasma frequency is determined by charge carrier mobility. A high mobility is connected with a very steep rise, whereas a low mobility represents a slow rise of the reflectivity.

By proper fitting the dielectric function of the material to the measured spectra, it is possible to obtain charge carrier concentration and mobility from the spectral data. The sheet resistance of the films can than be calculated by using the specific resistance and the film thickness determined from the interference pattern of the reflectance spectra. Layer systems can be analysed by mathematically evaluating the spectra with the aid of the plan parallel plate model for layer systems.

The shape of the plasma reflection edge is also an indication of the quality of the thin film material investigated. A perfect film with a low number of defects has charge carriers with high mobility and , thus, a steep rise of reflectivity at the plasma frequency. A large number of defects or many grain boundaries lead to charge carrier scattering at and with this to a flat rising reflectivity at the plasma frequency.

Fig. 2 shows an example for an experimental and a fitted curve using the mathematical Drude-Lorentz model for an ITO film on glass.

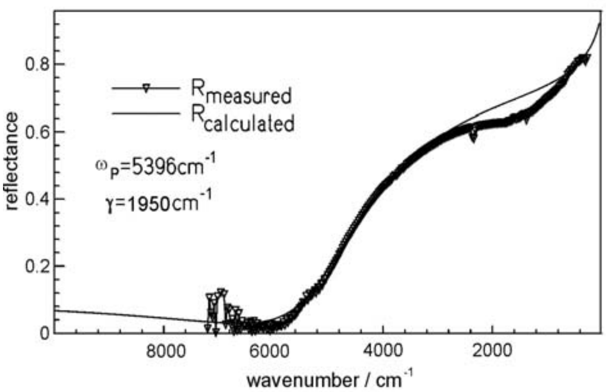

Fig. 2. Fitting of the calculated reflection spectrum by variation of ω_p and γ to an experimental measured one of a 440 nm dc-O_2-sputtered ITO-film [2]

An approximate determination of the plasma frequency for thin film quality control is also possible by taking the wavelength of the minimum reflectivity near the plasma reflection edge.

2.4 Software package "Optech Plasmon Calculations"

A software package called "Optech Plasmon Calculations" is in development at Gesimat (Figure 3).

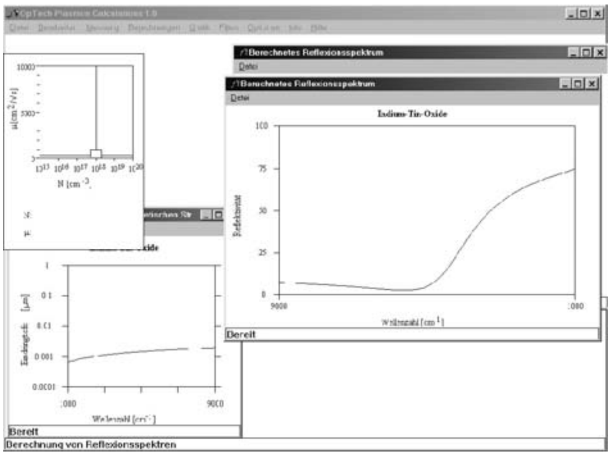

Fig. 3. Gesimat program "Optech Plasmon Calculations" (screen shot, German version)

3. Examples

3.1 TCO coated glass

It has been shown by several authors that TCO films on glass can be characterised by reflection spectroscopy [e.g. 2-6]. The next two examples show that this method can be applied to control the quality of TCO films during coating (ITO) or thermal processing (FTO) of the films.

3.1.1 ITO coated glass

ITO is the most popular transparent conducting oxide. In comparison to FTO it can reach lower sheet resistances at comparable thickness and it can easily be etched for display applications and the like because it is chemically not that stable as FTO.

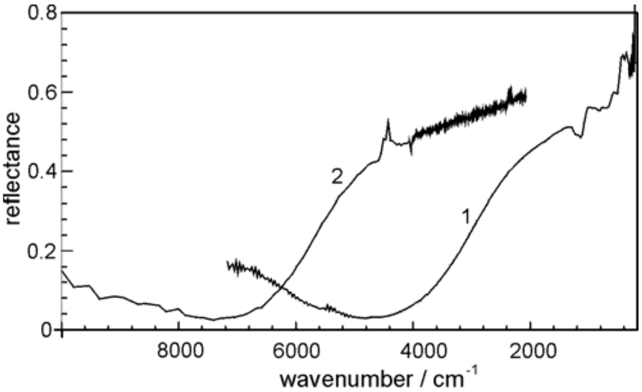

Fig. 4. Reflection spectra of ITO thin films produced at different sputtering conditions: 1 – dc-O_2-sputtered , 2 – dc-H_2O-sputtered [2]

The properties of ITO layers produced at different sputtering conditions can very well be characterised by their reflection spectra in the range of the plasma reflection edge [2]. This can be seen from Fig. 4 which shows the reflection spectra of 2 ITO films deposited by reactive dc sputtering from an In/Sn alloy target with a composition of In/Sn= 80/20 Ma% under different sputtering conditions.

The shift of the plasma edge to higher wavenumbers detects a higher free carrier concentration of dc-H_2O-sputtered ITO-films compared to dc-O_2-sputtered ones. The ascent of the reflectivity appears nearly equal at dc-O_2- and dc-H_2O-sputtered ITO-films and indicates comparable charge carrier mobility.

3.1.2 FTO coated glass

Fluorine-doped tin oxide films are coated onto glass substrates in order to provide transparent conducting films or highly stable heat reflection films. The heat reflection properties of FTO are directly connected with the plasma reflection edge. The plasma reflection edge of FTO lies in the NIR spectral range (see Fig. 5).

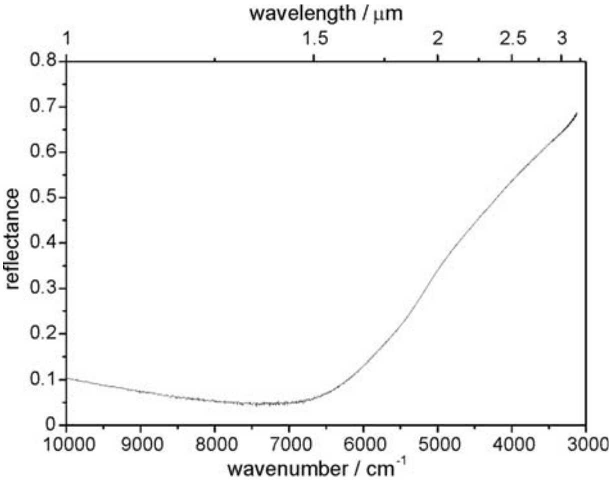

Fig. 5. Reflection spectrum of FTO coated glass in the area of the plasma reflection edge

During the production of heat strengthened or toughened glass the material is subjected to enhanced temperatures around 640°C. If during the production process the FTO coated glass has experienced a too high temperature the conductivity of the FTO coating decreases. This can also be measured by a shift of the plasma reflection edge.

In this example we measured only the wavelength of the reflectivity minimum near the plasma reflection edge for evaluation of film quality changes. FTO coated glass with a sheet resistance of 17 Ω/□ before tempering has its reflectivity minimum at 1350 nm. In samples which had an increased sheet resistance of up to 26 Ω/□ after tempering the reflectivity minimum was shifted by up 70 nm to 1420 nm.

As can be seen from this example the reflectivity measurement is a control parameter during processing steps of TCO coated glass.

3.2 Thin aluminium films

The plasma reflection edge for most bulk metals lies in the UV spectral range because of their high charge carrier concentration.

One of the authors (MR) developed a procedure to monitor the quality of evaporated aluminium thin films on single crystalline $LiNbO_3$ wafers by measuring the reflectance of the Al films directly after coating in the wavelength range between 200 and 400 nm and comparing this spectrum with a reference spectrum. The aluminium films had a thickness of about 350 nm. This monitoring procedure is in use at a larger German manufacturer of electronic components for more than 10 years now, with very good results.

In the glass industry this method could be employed to control the quality of low-e and mirror coatings.

3.3 Semiconductors: n-GaAs

The measurement and subsequent evaluation of the reflection spectra in the range of the plasma frequency has been used frequently for the characterisation of semiconductor materials [7, 8]. An example for the quality control of a semiconductor material is the characterisation of n-GaAs after neutron irradiation and during the following thermal annihilation of neutron irradiation induced effects [8].

Neutron irradiation of semiconductors is performed for so-called neutron-transmutation doping or for neutron activation analysis experiments. Neutron irradiation induces defects which significantly alter the properties of single-crystalline semiconductors. This can be detected by reflection spectroscopy.

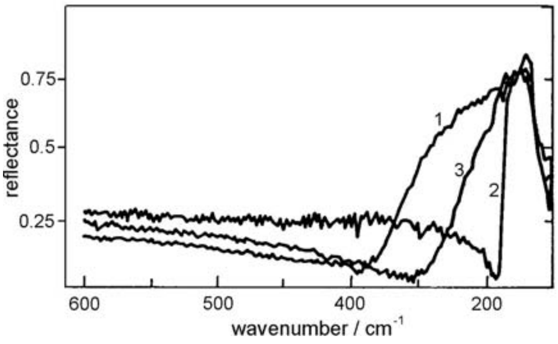

Fig. 6. Reflection spectra of n-GaAs before (1) and after neutron irradiation (2) and after thermal annihilation of neutron irradiation induced defects (3) [8]

In the example presented in this paper, the n-GaAs had a charge carrier concentration of $1 \cdot 10^{18}$ cm^{-3} before neutron irradiation calculated from spectrum 1 in Fig. 6. After neutron irradiation no plasma reflection edge can be measured only the phonon excitations (spectrum 2). This is because neutron irradiation induced defects trap nearly all of the free charge carriers and the free charge carrier concentration is therefore very low. Many defects can be annihilated by thermal treatment. Spectrum 3 shows the reflection spectrum after thermal treatment at 650°C. The charge carrier concentration is now $6.9\cdot10^{17}$ cm^{-3}. This means many but not all defects could be annihilated.

Thin semiconductor films are coated on glass for photovoltaic applications. Examples are CdTe or $CuInS_2$. The reflectance spectroscopy in the appropriate wavelength range could be used for quality control of such films too.

3.4 Electrochromic thin films: WO_3

The use of the reflection spectroscopy method for the investigation of crystalline electrochromic WO_3 has been investigated by Granqvist [9].

In crystalline tungsten oxide films the electrochromic behaviour (i.e. coloration and bleaching) is connected with a shift of the plasma reflection edge. In the bleached uncoloured state the plasma reflection edge is positioned in the infrared spectral range. Coloration by electrochemical reduction of crystalline tungsten oxide is accompanied by a shift of the plasma edge into the visible part of the spectrum. This is due to the formation of additional charge carriers which lead to a higher plasma frequency. This process is reversible.

However, if disordered amorphous tungsten oxide films are used in electrochromic devices, the coloration of tungsten oxide is due to the formation of colour centers and no significant change in the reflection spectrum occur. This is the case in the Gesimat-type electrochromic device [10].

3.5 Titanium dioxide films

Among the film materials characterised by reflectance spectroscopy in the range of the plasma frequency are also TiO_2:Ti films [11]. These films are prepared as absorber layer materials for infrared thermal detectors.

In the glass industry titanium dioxide films are of interest as photocatalytic coating or as part of dye sensitised solar cells (DSSC).

3.6 Conducting polymers

Conducting polymers such as polyaniline or polythiophenes are currently considered for many applications. Some of conducting polymers also have electrochromic properties, with advantages in switching speed and the variety of attainable colours compared to inorganic materials. Therefore, they are also of interest in the glass industry.

The properties of conducting polymer films can also be investigated by measuring their reflectance spectra in the spectral region of the plasma reflection edge [12].

3.7 Doped diamond films

Although pure diamond is a very good insulator, it can be made conducting by doping with e.g. boron impurities leading to a p-type semiconductor. Doped diamond films can be used for different purposes among them the use as an electrode material in the water treatment industry [13]. In the glass industry diamond films are discussed as a scratch resistant film to protect glass against vandalism as it can be seen everyday in the glazing of vehicles of the public transportation system. Diamond-like carbon (DLC) coatings have already been introduced for this purpose. Diamond films would have an even larger anti-scratch effect.

Again it is possible to evaluate the properties of doped diamond films by use of reflectance spectroscopy [14].

4. Conclusion

The reflectance spectroscopy method in the spectral range of the plasma reflection edge can be applied to all materials with a certain electronic conductivity. Insulators cannot be investigated by this technique. However, many materials which are used in the glass industry as a thin film material on glass are conducting.

At Gesimat at lot of experience in the practical application of the reflectance spectroscopy method for the determination of the quality of materials has amounted. This concerns thin metal films, semiconductors and transparent conducting oxides. However, this versatile method can be expanded to the investigation of a multitude of other materials too. It's more widespread use in the glass industry could help to improve process and quality control.

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