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## Optical method for homogeneity testing of thin films electrodes for photovoltaic cells

**Abstract.** The new non-destructive, optical method for homogeneity of photovoltaic cells testing is presented. The uniformity of thickness and optical constants of the deposited large area electrodes (15.6\*15.6 cm\*cm) were measured by spectroscopic ellipsometry. The sputtering deposition equipment for metallic electrodes (Al, Mo) was designed and run. The ALD equipment was used for transparent electrodes deposition (ZnO:Al). Description of vacuum deposition systems as well as tests resultants are presented.

**Streszczenie.** Przedstawiono nową, nieniszczącą, optyczną metodę badania jednorodności ogniw fotowoltaicznych. Jednorodność grubości i stałych optycznych osadzonych elektrod o dużej powierzchni (15,6\*15,6 cm\*cm) zmierzono metodą elipsometrii spektroskopowej. Zaprojektowano i uruchomiono urządzenie do napyłania jonowego elektrod metalicznych (Al, Mo). Do osadzania elektrod przezroczystych (ZnO:Al) zastosowano urządzenie ALD. Przedstawiono opis systemów do napyłania próżniowego oraz wyniki badań. Optyczna metoda badania jednorodności cienkowarstwowych elektrod do ogniw fotowoltaicznych.

**Keywords:** homogeneity test, PV cells,

**Słowa kluczowe:** fotowoltaika.

### Introduction

The problem of deposition of different types of electrodes for PV cells is important and solved on a different way. Several techniques of deposition are used nowadays, e.g., atomic layer deposition (ALD) for ZnO:Al (AZO) [1, 2] and DC sputtering technique (PVD) for Mo and Al.

One of the important parameters is homogeneity of thickness and optical parameters of deposited electrodes. Both were measured by spectroscopic ellipsometry - very sensitive method. This method has two steps. First measuring ellipsometric angle and the second one is fitting data to a physical model of deposited film or film system. Different types of electrodes were deposited and homogeneity of thickness and optical constant were tested by mapping the electrodes surface by spectroscopic ellipsometry. The spot light was focused to 0.1mm and thickness and refractive index were measured with small step over the electrodes surface. The 3D maps of measured parameters are presented in this paper. Proposed test is time consuming for large area cells but could be used by producers of different types of photovoltaic cells as a final step before running production.

### Deposition

Metal electrodes were deposited in a vacuum DC sputtering device from a large metallic targets e.g. Al, Mo, Ti with a diameter of 140 mm [3, 4].



Fig. 1. Home made vacuum equipment for large area metallic electrodes deposition.

This allows the metal electrode to uniformly cover the entire surface of a 15.6x15.6 cmxcm silicon solar cell. The design of the device is shown in Figure 1. The deposition

process is fully automated and can be carried out in library program mode or by manual input of process parameters. An image of the operator panel is shown in Figure 2 and Figure 3.



Fig. 2. System operator desktop (PVD) with fields for entering process data.

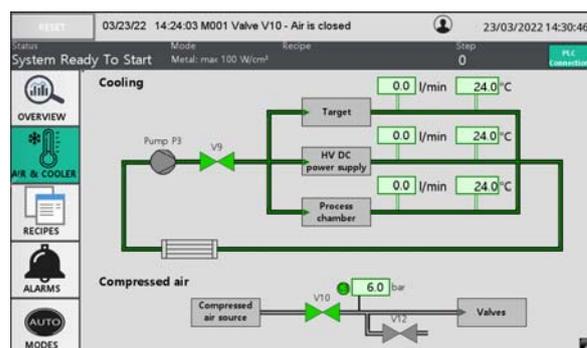


Fig. 3. System operator desktop (PVD) with the ability to manually activate system components.



Fig. 4. ALD reactor BENEQ P400, used for the deposition of thin transparent electrodes.

The ALD equipment was used for transparent electrodes deposition (ZnO:Al) (Fig.4) while the DC sputtering method was used to produce layers of Al and Mo (Fig.1).

### Measurements

At large-scale production, for elements (photovoltaic cells) that will work for 20-30 years, stability of all parameters is important, and the most important is the efficiency of energy conversion. In the production process during electrode deposition possible inhomogeneities, for example thicknesses, can cause inhomogeneous current flow and consequently formation of so called hotspots resulting in reduced efficiency or even destruction of the cell.

Spectroscopic ellipsometry (Woollam Co., Inc, M-2000 J.A. RAE ellipsometer) was chosen as a non-destructive method to study photovoltaic cells [5].

For mapping over large areas, an ellipsometer upgrade is necessary to install collimators that focus the beam to a diameter of 140  $\mu\text{m}$ . The second indispensable element is the software that allows automatic measurements of the whole surface of the sample according to the given algorithm. In case of large area samples (for a photovoltaic cell 15.6x15.6  $\text{cm}^2$ ) it is possible to select reasonably even 2 200 000 measurement points.

In the spectroscopic ellipsometry (SE) method, the measurement process is done in two steps [6], the first step is to measure the ellipsometric angles Psi and Delta. The second is the selection of the optical model for the material type.

The measurement results are shown in Fig. 5. For better model fitting, 4 incidence angles of 60°, 65°, 70° and 75° were used. The measurement results are the red line for Psi angle and the green line is Delta, while the black dots are the mode fitting results.

During the measurements, two ellipsometric parameters were recorded: Psi, which is the amplitude ratio for polarizations *s* and *p* before and after reflection from the sample, and Delta, which is the phase shift between the components of the reflected light in the parallel *s* and perpendicular *p* planes, before and after reflection [5]. The angle between the *p* and *s* vectors was 45°. Ellipsometry records the change in polarization of light after reflection from the sample (1):

$$\rho = \frac{r_p}{r_s} = \tan(\text{Psi}) \cdot \exp(i \cdot \text{Delta}) \quad (1)$$

The fraction in the above equation is the ratio of the complex Fresnel reflectance of the sample for *p*- (in the plane of incidence) and *s*- (perpendicular to the plane of incidence) polarized light [7]. The measurement is made as a function of wavelength and angle of incidence. This method is very accurate and does not require a reference material.

A model analysis of the dispersion dependence of Psi( $\lambda$ ) and Delta( $\lambda$ ) is necessary to obtain relevant data. A suitable theoretical model allows predicting the film thickness and the optical constants refractive index and extinction coefficient [7, 8, 9]. These quantities characterize the surface homogeneity very well. In the program, the mean square error (MSE) is used to quantify the difference between experimental and predicted data [10].

The materials of interest in this paper, are dielectrics [1, 5, 6], essentially transparent in the SE wavelength range of measurement. For such materials, the extinction coefficient is close to zero,  $k \approx 0$ . Due to the size of the energy gap

lower for semiconductors, they absorb short wavelength light and transmit long wavelength light.

In the wavelength range where the layer is transparent, light can penetrate the layer and provides information about its thickness. For transparent materials, Cauchy's formula for the spectral dependence of the refractive index is used (2):

$$n(\lambda) = A + B + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (2)$$

where: *A*, *B*, *C* are Cauchy coefficients determined from regression analysis and are given in m.

The Cauchy equation assumes  $k = 0$  and can be applied to dielectrics and organic materials. It was further developed by Woollam [5].

For semiconductors, Cauchy's formula is applicable for photon energies smaller than the absorption edge.

However, for small absorption in the layer, the Cauchy relation can be used. For absorbing layers, the dispersion of the extinction coefficient  $k(\lambda)$  is given by Urbach's relation (3):

$$k(\lambda) = \alpha \cdot \exp\{\beta(E - E_g)\} \quad (3)$$

where: *E* is the photon energy,  $\alpha$ - amplitude,  $\beta$ - an exponent factor,  $E_g$  the energy band gap of the layer.

Equation (3) describes a small, exponentially decreasing absorption below the band gap, characteristic of many amorphous materials [9, 4].

A model analysis of the  $n(\lambda)$  and  $k(\lambda)$  dispersion relationships is necessary to obtain the relevant data. A suitable theoretical model can predict them and as functions of optical constants and film thickness. The mean square error (MSE) is used to quantify the difference between experimental and predicted data [11].

When the material is absorbing, the Cauchy equation cannot be used. Commonly used models for absorbing materials are oscillator and b-spline models. The b-spline models are beneficial when describing complex optical relationships.

In oscillator models, one of which is used in this paper, the peaks of the optical constants that appear at resonant frequencies are described by various oscillator equations. Simple oscillators include Gaussian, Lorentz, and harmonic oscillators. A simple Gaussian oscillator describes the absorption shapes using 4 parameters, i.e., the energy of the medium (related to the resonant frequency), amplitude, broadening, and offset shifting [12]. Several asymmetric oscillators have been proposed for amorphous materials with an energy gap and no absorption at lower energies, among others, including Cody-Lorentz and Tauc-Lorentz models.

A very useful parameterization of the optical functions of amorphous dielectrics and semiconductors was proposed by Jellison and Modine. This model is now referred to as the Tauc-Lorentz model because it is based on a combination of the Tauc absorption edge and oscillator broadening as by the Lorentz oscillator [7, 8].

The Tauc model predicts the absorption coefficient  $\alpha = 4\pi k/\lambda$ ,  $f = c/\lambda$  (*c* - speed of light in vacuum) as (4):

$$\alpha = M^2 \frac{(h\nu - E_{Tauc})^m}{h\nu} \quad (4)$$

where: *M* contains all the Gaussian simple constants. The energy  $E_{Tauc}$  is the Tauc gap energy, which is a measure of

the band gap in amorphous materials. The power  $m$  depends on whether the material is crystalline ( $m = 3/2$ ) or amorphous ( $m = 2$ ).

According to Tauc's relation, the plot of  $(\alpha h\nu)^{1/m}$  against the photon energy  $h\nu$  is linear in some spectral region. The extrapolation of this straight line intersects the  $(h\nu)$ -axis, which gives the energy gap value [13, 14].

The Cauchy model was used to determine the refractive indices and extinction coefficients of the layers. Such layers are non-absorbing dielectrics with coefficients  $k \approx 0$  and  $n$  given in equation (2).

Therefore, the Tauc-Lorentz model is more suitable for fitting it to the results of ellipsometry measurements. Figure 5 shows the results of fitting the models to the experimental data.

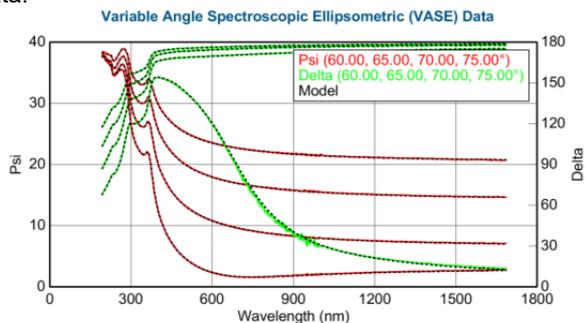


Fig. 5. Plot of Psi and Delta ellipsometry data for varying spectrometric angles fitted by the model marked with black dots

The dispersion functions of the refractive index  $n(\lambda)$ , and the extinction coefficient  $k(\lambda)$ , determined for the layers given as functions of wavelength, are shown in Figure 6.

Clear quantitative differences can be seen. The spectral dependence of the refractive indices shows normal dispersion typical of transparent dielectric materials.

Both refractive indices and extinction coefficients increase in the spectral range 1600 to 400 nm. These changes are due to the increase in the absorption of the films. The observed differences may indicate a transformation of the electron structure of the films from a typical dielectric to a semiconductor. This may be parallel to the increase in the density of the films due to annealing, which explains the increase in the refractive index according to the formula (5):

$$(5) \quad C_{DG} = \frac{n-1}{\rho}$$

The above equation is the Gladstone-Dale formula [12, 15, 16], which relates the average refractive index of a medium,  $n$ , to its density, where CDG is the Gladstone-Dale coefficient [17, 18].

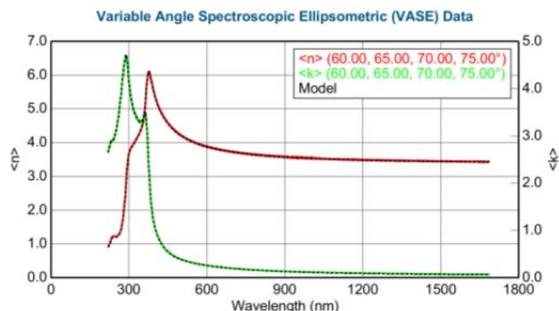


Fig. 6. Graph of  $n$  and  $k$  dependencies depending on the wavelength

Implementation of the measurement algorithm for the whole surface of the sample with any number of measurement points allows to determine the spatial map of any chosen parameter ( $n$ ,  $k$ ,  $d$ ). The homogeneity map for the extinction coefficient in the ZnO:Al sample of size  $0.5 \times 0.5$  cm<sup>2</sup> is shown in Figure 7. On the basis of the presented data (Fig. 7) one can state high sensitivity of the method and homogeneity of the tested surface.

The method gives similar results as atomic force microscopy (AFM) but not on the surface of a few microns but on the surface of several cm. It means that it is useful for macroscale samples, especially for photovoltaic cell electrodes.

The presented data show high accuracy of the measurements.

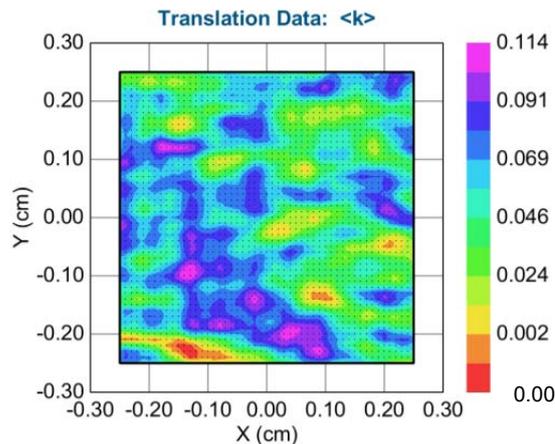


Fig. 7. Diagram of the distribution of the extinction coefficient on the sample surface for wavelength  $\lambda = 900$  nm

The extinction coefficient uniformity map for a ZnO:Al coated photovoltaic cell for a size of  $0.5$  cm x  $0.5$  cm is shown in Figure 7, and the refractive index  $n$  uniformity map for the same sample for a size of  $15.6$  cm x  $15.6$  cm is shown in Figure 8.

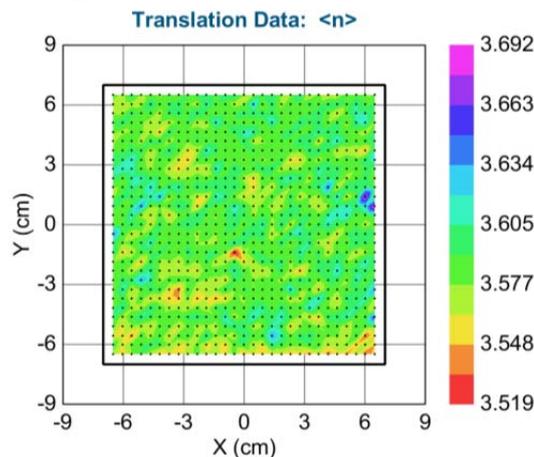


Fig. 8. Diagram of the refractive index distribution  $n$  for wavelength  $\lambda = 600$  nm on the sample surface ( $15.6 \times 15.6$  cm<sup>2</sup>)

The refractive index distribution diagram can be represented in 3D (Fig. 9), similarly as it is done for AFM images, only on a larger scale. In Figure 9 one can see slight inhomogeneities at the edges of the sample.

These inhomogeneities are relatively large in Fig. 9 because of the scale that was adopted for the refractive index  $n$  axis. For a better illustration of the measurements carried out, a drawing of the thickness distribution of the tested surface depending on the position was made (fig. 10). From it, it can be clearly seen that the uniformity of the

layer thickness (70 nm, with an accuracy of 4.3%) is maintained over the entire surface.

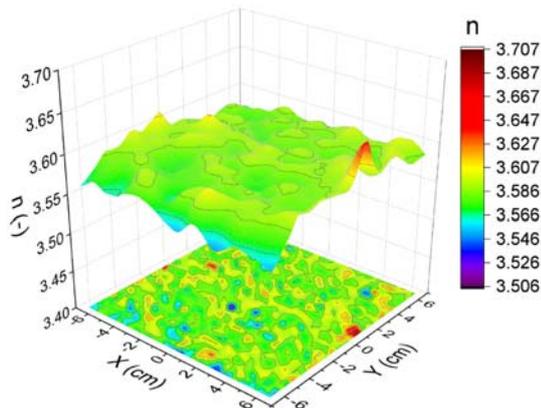


Fig. 9. Distribution of refractive index uniformity on the surface of a 15.6x15.6 cmxcm silicon wafer

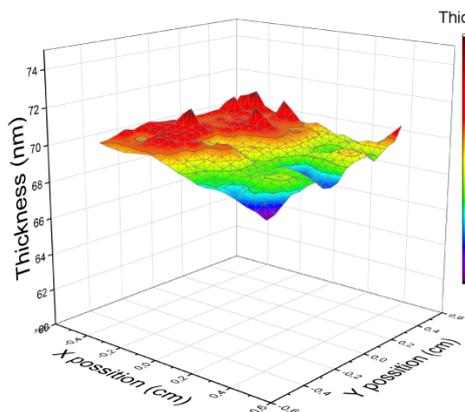


Fig. 10. Diagram of the thickness of the sample (sample thickness about 70 nm).

## Conclusions

This paper presents two vacuum systems for deposition of large area electrodes for PV cells. First one its homemade DC sputtering equipment for metallic electrodes (Al, Mo). Second one its commercial reactor ALD BENEQ P400 for transparent electrode deposition.

The non-destructive optical method of measuring the homogeneity of the parameters of the obtained films such as thickness and optical constants it means the extinction coefficient and refractive index is also described.

The presented measurement results allow to accurately assess both in 2D and 3D the homogeneity of evaluated parameters. In contrast to microscopic methods, e.g. AFM, the optical method allows to analyze large samples, e.g. electrodes for a photovoltaic cell of standard dimensions of 15.6 cm x 15.6 cm. The method can be particularly useful for photovoltaic cell manufacturers.

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