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SPECTRAL ELLIPSOMETRY ANALYSIS OF ULTRATHIN AMORPHOUS SILICON LAYERS

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ABSTRACT: Ultrathin layers of hydrogenated amorphous silicon (*a*-Si:H) are of high interest in today's photovoltaics. A reliable characterization (layer thickness, optical constants) of such layers is essential for process control and development. Spectral ellipsometry is a fast and non-destructive method for analyzing thin layers. A common analysis procedure for ellipsometric data fails in case of ultrathin *a*-Si:H layers with thicknesses below 15 nm. For evaluation of such *a*-Si:H layers a new analysis procedure has been introduced. The procedure has been applied successfully to layers of a thickness down to 5 nm, verified by reflection and transmission measurements as well as transmission electron microscopy.

Keywords: spectral ellipsometry, a-Si, PECVD

1 INTRODUCTION

Ultrathin hydrogenated amorphous silicon (*a*-Si:H) layers with thicknesses below 15 nm have several applications in today's photovoltaics. Representative examples are front side passivation of silicon solar cells [1] or hetero-junction solar cells (HIT) [2]. To develop such *a*-Si:H-based devices a reliable characterization is essential for determining layer thickness and optical properties of the *a*-Si:H layer. In general, the optical properties of *a*-Si:H are influenced by deposition parameters, e.g. substrate temperature [3]. Especially in case of ultrathin layers optical properties can also be affected by the layer thickness [4]. A fast and non-destructive standard method for determining layer thicknesses and optical properties (refractive index *n*, absorption *k*) is ellipsometry. Since ellipsometry is not a direct measurement, layer thickness and optical constants have to be fitted to the measured ellipsometric data using optical models. The choice of the optical model and especially the choice of suitable starting values for the respective model parameters have a crucial impact on the fit validity. Therefore an analyzing procedure is required which offers suitable start values for analyzing ellipsometric data of ultrathin *a*-Si:H layers with *unknown* optical properties.

A common procedure for evaluation of ellipsometric data of thin *a*-Si:H layers fails in case of ultrathin layers (<15 nm). This work presents an analyzing procedure for characterization of ultrathin *a*-Si:H layers with unknown optical properties using spectral ellipsometry and common optical models for data evaluation.

2 EXPERIMENTAL

The *a*-Si:H layers were deposited using a radio frequency (13.56 MHz) parallel plate PECVD reactor with a mixture of SiH_4 and H_2 as precursor gases. Shiny etched FZ silicon wafers were used as substrate material. Before deposition, the FZ Si samples were wet-chemical cleaned using a HNO_3/H_2O dilution followed by an HF etch. The *a*-Si:H layers were deposited directly on the FZ Si substrate as well as on a 105 nm thick thermally grown SiO_2 layer.

A spectral ellipsometer (J. A. Woolam) with a spectral range of 250–1000 nm was used for *ex situ* ellipsometry measurements. Each sample was measured at three angles of incidence (65°, 70°, 75°) to have sufficient ellipsometric data for modeling. Furthermore 40 spectra were taken and averaged for every ellipsometric data measurement to improve the signal to noise ratio. Data acquisition and analysis was performed using WVASE32 software (version 3.650).

TEM studies for layer thickness reference measurement were performed using a FEI Titan 80-300 system at an accelerating voltage of 300 kV.

Reflection and transmission measurement were performed using a spectrophotometer (Cary 500i) with a spectral range of 250–2500 nm in order to have a reference measurement for the optical constants.

3 ANALYZING PROCEDURE

3.1 Used Optical Models

Ellipsometry measures the phase change of a polarized light beam due to the reflection at the coated surface of the sample. This change in phase is characterized by the ratio of the total reflection coefficients [5]:

$$\rho = \frac{R_p}{R_s} = \tan\psi\, e^{i\Delta} \qquad (1)$$

where R_p and R_s are the Fresnel reflection coefficients for light polarized parallel and perpendicular respectively to the plane of incidence. In ellipsometry the measured quantities are expressed in ψ and Δ. ψ characterizes the amplitude and Δ the phase of the reflected light beam.

In order to calculate the desired values (e.g. layer thickness, optical constants) from the measured data, a suitable optical model has to be applied. For amorphous semiconductors several models exists [4, 6-8]. In the present work the widely accepted Tauc-Lorentz (TL) model [8] is applied, a specific model for amorphous semiconductors based on the Tauc relation [9]. In ellipsometry the optical properties are often represented by the dielectric function $\varepsilon = \varepsilon_1 + \mathrm{i}\,\varepsilon_2$, which is directly linked to *n* and *k*, the refractive index and the extinction coefficient. The complex part of the dielectric function for the TL model is given by

$$\varepsilon_2(E) = \frac{A\,E_0\,C\left(E-E_g\right)^2}{\left(E^2-E_0^2\right)+C^2E^2}\cdot\frac{\Theta\left(E-E_g\right)}{E} \qquad (2)$$

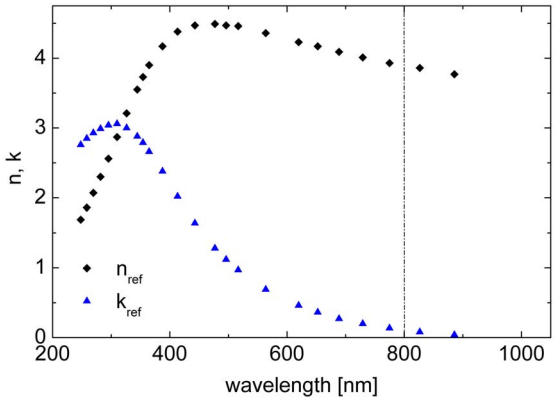

Fig. 1: Refractive index n_{ref} and extinction coefficient k_{ref} of amorphous silicon according to Ref. 10.

where $\Theta(x)$ is the Heaviside function. The real part is calculated by integrating the Kramers-Kronig relation given by

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi\, \varepsilon_2(\xi)}{\xi^2 - E^2}\, d\xi \qquad (3)$$

where P is the Cauchy principal part of the integral. In both expressions E_g, A, E_0, C and $\varepsilon_1(\infty)$ are treated as independent fit parameters. E_g can be interpreted as the optical band gap according to the definition of Tauc *et al.* [9].

Besides the *a*-Si:H layer, the crystalline silicon (*c*-Si) and the thermal grown SiO_2 layer have to be modeled for the evaluation of the ellipsometric data. Since both materials are optically well known, they are modeled by using tabulated data for *n* and *k* according to Ref. 11.

3.2 Procedure for Analyzing *Thin a*-Si:H Layers

A reasonable optical model has several fit parameter. In case of the TL model there are six independent fit parameters including the layer thickness. Since their start values for fitting can have a crucial impact on the fit results, it is necessary to have a good estimation of the start values when analyzing *a*-Si:H layers with unknown optical constants. Such estimation is done in the first three steps of the following familiar analysis procedure by using a simple optical model.

1: First, a simple model using as few fit parameters as possible is applied to get a rough estimation of layer thickness and optical constants. Such a model is the Cauchy model, an optical model for transparent matter. Since *a*-Si:H is approximately transparent above 800 nm (Fig. 1), this model can be applied for the spectral range above 800 nm.
2: In order to get a rough estimation of the optical constants for the whole measured spectral range (250 – 1000 nm), next a point-by-point fit based on the Cauchy parameters is performed. The fit starts at 1000 nm using the *n* and *k* values of the Cauchy model as first start values. The layer thickness is kept constant at the value obtained by the Cauchy fit. The *n* and *k* values of the *a*-Si:H layer are calculated for each wavelength independently, always using the prior results as starting values.

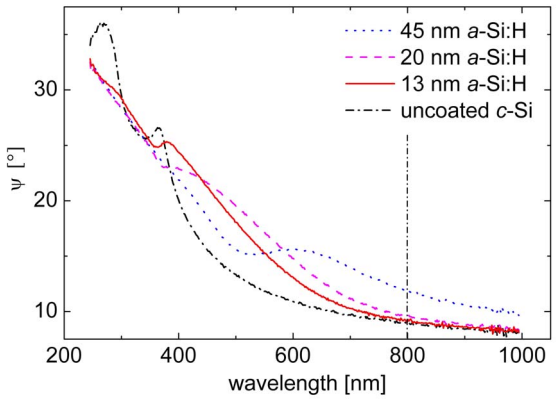

Fig. 2: Measured ψ values for an 13, 20 and 45 nm thick *a*-Si:H layer deposited on *c*-Si substrate compared to the data measured on uncoated *c*-Si. In this case ψ is measured at an angle of incidence of 70°.

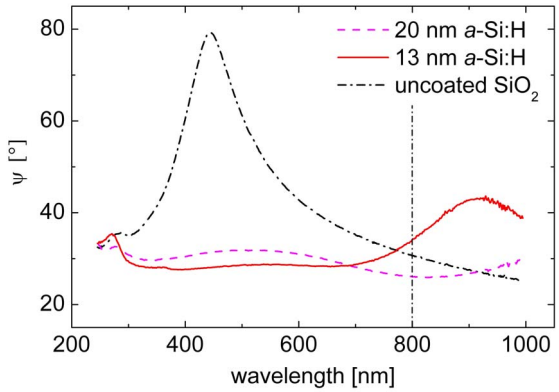

Fig. 3: Measured ψ values for an 13 and 20 nm thick *a*-Si:H layer deposited on a 105 nm thermally grown SiO_2 layer compared to the data measured on the uncoated SiO_2 layer. ψ data is shown for an angle of incidence of 70°.

3: The results of the prior step are a rough estimation of *n* and *k* for the *a*-Si:H layer over the whole measured spectral range. In order to apply those results to the TL model, i.e. the start values for its fit parameters, the TL model is adapted to those *n* and *k* values by adjusting the fit parameters. This could be done by fitting the TL model to the *n* and *k* values.
4: The prior step leads to a rough estimation of the fit parameters for the TL model. This values are now used as start values for fitting the total layer system – containing the TL model for modeling the *a*-Si:H layer – to the measured ellipsometric data. In this final fit the thickness of the *a*-Si:H layer is treated as a fit parameter again using the value obtained in the first step as start value.

In the non-absorbing wavelength range above 800 nm, the signal contrast between the ellipsometric data of the uncoated *c*-Si substrate and the *a*-Si:H layer decreases with decreasing layer thickness and vanishes for an *a*-Si:H thickness below ~15 nm (see Fig. 2). Thus the first part of the analyzing procedure – the application of the Cauchy model in the non-absorbing wavelength range above 800 nm – fails. Fig. 2 shows exemplary the

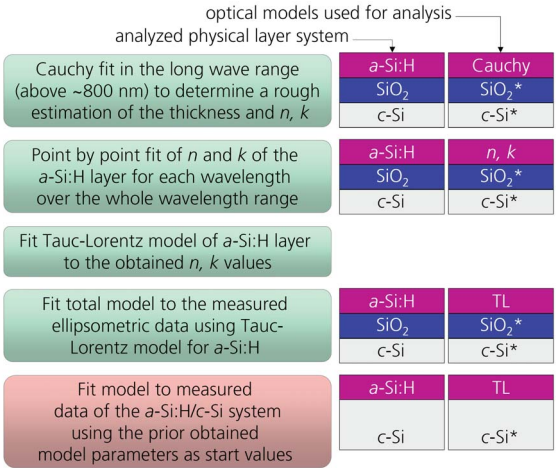

Fig. 4: Flow chart of the fitting procedure for ultrathin *a*-Si:H layers. The applied layer structure and the used optical model are shown on the right. Layers marked with a * are model by tabulated data.

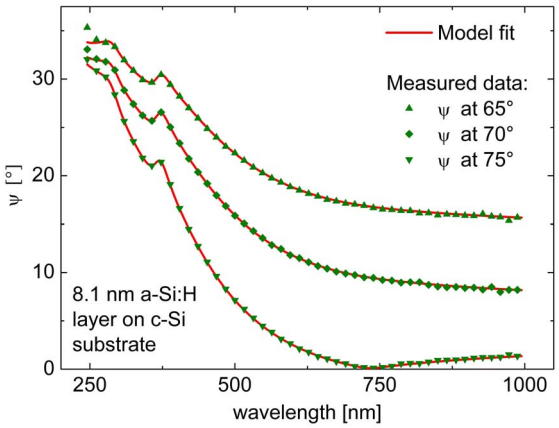

Fig. 5: Measured and modeled ellipsometric data of a 8.1 nm thick *a*-Si:H layer on *c*-Si substrate. Data is shown for different angles of incidence. Modeling has been done corresponding to the presented modeling procedure. A very good agreement between measured and modeled data is obtained.

ellipsometric data ψ. Through this work always only ψ data is shown, analogous holds for the Δ data too.

An intermediate thermal grown SiO_2 layer between the ultrathin *a*-Si:H layer and the *c*-Si substrate is known to increase that signal contrast. In this case there is also in the non-absorbing wavelength range a strong signal contrast (see Fig. 3) and the analysis procedure (now for the *a*-Si:H/SiO_2/*c*-Si system) can be applied again. However, especially in case of ultrathin layers, the substrate can have an influence on the growth of the *a*-Si:H. Thus, it is preferable to be able to measure and analyze the original *a*-Si:H/*c*-Si system. A procedure for measuring and analyzing the ellipsometric data of the *a*-Si:H/*c*-Si system is presented in the next chapter.

3.3 Procedure for Analyzing *Ultrathin* *a*-Si:H Layers

This procedure takes advantage of the intermediate SiO_2 layer for analyzing ellipsometric data of the *a*-Si:H/*c*-Si system. Thus, for this procedure it is necessary to have *a*-Si:H deposited on the *c*-Si substrate – the sample of interest – as well as on the SiO_2/*c*-Si system. The modified procedure for analyzing ultrathin *a*-Si:H is given by following two steps (compare Fig. 4):

1: The measured ellipsometric data of the *a*-Si:H/SiO_2/*c*-Si system is analyzed analogous to the procedure described in section 3.2. The difference is only the inserted intermediate SiO_2 layer which is modeled with a constant thickness and tabulated optical constants in order to have as few fit parameters as possible. Therefore the SiO_2 layer is characterized before the *a*-Si:H deposition.
2: The results of step 1 are the parameters of the TL model and the layer thickness for the *a*-Si:H layer on SiO_2. This results are used as start values for the global TL model fit of the *a*-Si:H/*c*-Si system.

We applied this procedure to a set of 26 samples coated with ultrathin *a*-Si:H layers with thickness between 5-20 nm. For all investigated samples this procedure led to a good agreement between measured and calculated ellipsometric data, characterized by small confidence limits for the model parameters. The confidence limits are results of the fitting procedure. In this work the standard 90% confidence limit definition is used. The evaluataion of the 26 samples led to an average relative confidence limit of 0.15% for the layer thickness. Fig. 5 shows the measured and calculated ellipsometric data for an 8.1 nm thick *a*-Si:H layer on *c*-Si.

However, the described procedure contains some assumptions and simplifications. First of all, the model contains a multitude of fit parameters. This can lead to ambiguities in the physical interpretation of the fitting results. Furthermore surface roughness or native oxides have not been taken into account to keep the total number of fit parameters small. Also the optical constants have been assumed to be constant over the whole thickness of the *a*-Si:H layer.

In order to verify the fit results and hence the assumptions and simplifications mentioned above, independent reference measurements for the layer thickness as well as the optical constants were performed.

4 REFERENCE MEASUREMENTS

4.1 Optical Constants

The optical constants were determined by performing reflection and transmission (RT) measurements of an *a*-Si:H layer deposited on a transparent sample (glass). The optical constants of the *a*-Si:H layer were calculated from a two-layer model containing the absorbing *a*-Si:H layer on a thick substrate. A native oxide on the *a*-Si:H layer was ignored. The substrate is assumed to be transparent and optical thick, i.e. the multiple reflections in the layer are incoherent. The *a*-Si:H layer is assumed to be optical thin (i.e. coherent multiple reflections). Calculations were performed according to Ref. [12] using a point-by-point fit for each wavelength.

To compare the ellipsometry analysis to the RT analysis an ultrathin *a*-Si:H layer was deposited in the same process on a glass substrate and on *c*-Si with and without SiO_2 coating. As the glass substrate is not com-

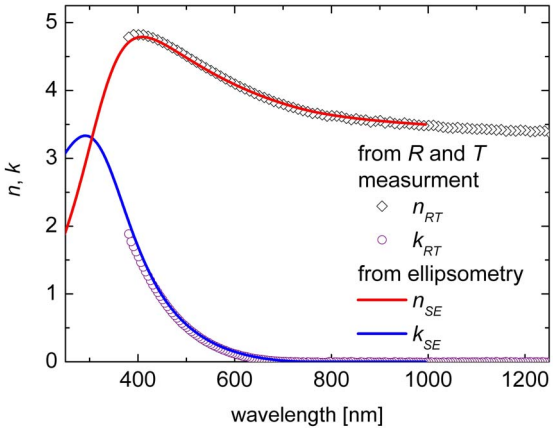

Fig. 6: Comparison of *n* and *k* for a 8.1 nm thick *a*-Si:H layer obtained from ellipsometry and RT analysis. The ellipsometry analysis was performed for an *a*-Si:H layer on *c*-Si substrate, the RT analysis for an *a*-Si:H layer on glass substrate. Both layers were deposited simultaneously.

pletely transparent below 400 nm the reference measurement only has been performed for wavelengths above 400 nm. Fig. 6 shows the optical constants of an 8.1 nm thick *a*-Si:H layer measured by ellipsometry and reflection and transmission measurement respectively. As can be seen, both measurements are in very good agreement. Thus the applied analyzing procedure for measurement of ultrathin *a*-Si:H layers is valid in case of optical constants.

4.2 Layer Thickness

To verify the layer thickness obtained by the described ellipsometry analysis the same sample (*a*-Si:H on *c*-Si) which has been used for the optical reference measurements is measured by TEM. Fig. 7 shows a cross-sectional transmission electron micrograph of this sample. The thickness of the *a*-Si:H layer can be determined to 8.3 nm by this micrograph. This is in excellent agreement to the 8.1 nm measured by ellipsometry. Thus it can be stated, that the analyzing procedure for characterization of ultrathin *a*-Si:H layers is valid.

5 CONCLUSIONS

Layer thickness and optical constants of ultrathin *a*-Si:H layers deposited by PECVD have been measured by *ex situ* spectroscopic ellipsometry. An analysis procedure, to analyze ellipsometric data of those ultrathin layers on *c*-Si has been introduced. The optical constants of *a*-Si:H are parameterized using the Tauc-Lorentz model. The procedure was applied to *a*-Si:H layers with thicknesses down to 5 nm. The obtained results for layer thicknesses were verified for exemplary samples using transmission electron microscopy. The optical properties were verified by transmission and reflection measurements. Thus it can be stated, that the analyzing procedure for characterization of ultrathin *a*-Si:H layers is valid.

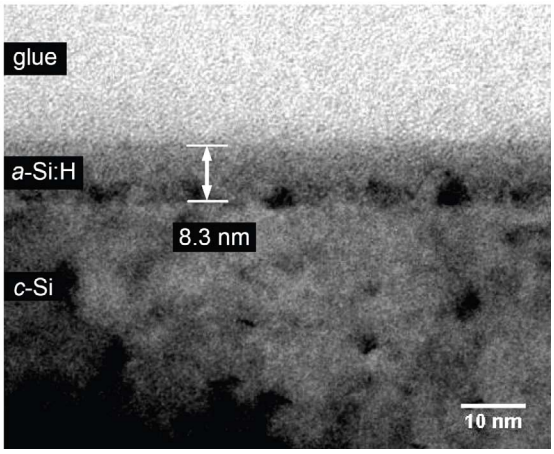

Fig. 7: TEM micrograph of the 8 nm thick *a*-Si:H layer deposited *c*-Si. Due to the TEM sample preparation there is glue on top of the *a*-Si:H layer. With the ellipsometric analysis a layer thickness of 8.1 nm was obtained.

6 ACKNOWLEDGEMENTS

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REFERENCES

[1] H. Plagwitz, Y. Takahashi, B. Terheiden, and R. Brendel, in Proceedings of the 21st European Photovoltaic Solar Energy Conference, Dresden, Germany, 2006.

[2] M. Taguchi, K. Kawamoto, S. Tsuge, T. Baba, H. Sakata, M. Morizane, K. Uchihashi, N. Nakamura, S. Kiyama, and O. Oota, Prog. Photovolt: Res. Appl. 8 (2000) 503.

[3] W. M. M. Kessels, R. J. Severens, M. C. M. van de Sanden, and D. C. Schram, J. Non-Cryst. Solids 133 (1998) 227.

[4] S. Hazra, M. Yamanaka, I. Sakata, and T. Tsutsumi, Jpn. J. Appl. Phys. 39 (2000) 6196.

[5] R. M. A. Azzam and N. M. Bashara, Ellipsometry and Polarized Light, North Holland Publishing Co., 1977.

[6] A. S. Ferlauto, G. M. Ferreira, J. M. Pearce, C. R. Wronski, R. W. Collins, X. Deng, and G. Ganguly, J. Appl. Phys. 92 (2002) 2424.

[7] A. R. Forouhi and I. Bloomer, Physical Review B 34 (1986) 7018.

[8] G. E. Jellison, Jr., F. A. Modine, Appl. Phys. Lett. 69 (1996) 371.

[9] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi 15 (1966) 627.

[10] D. T. Pierce and W. E. Spicer, Phys. Rev. B 5 (1972) 3017.

[11] E. D. Palik and G. Ghosh, Handbook of Optical Constants of Solids, Academic Press, 1998.

[12] H. A. Macleod, Thin layer optical filters, Taylor & Francis, 2001.