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Attn: Mrs. Zuzana Mrazkova

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Assessment and Review of the PhD Thesis „Modeling and characterization of materials and nanostructures for photovoltaic applications “ von Mrs. Zuzana Mrázková, MSc.

In order to give the PhD candidate the possibility to understand my questions and comments, this review report on the PhD thesis is written in English. I ask the candidate to comment during the defense on my comments and I also understand, if not all of my questions can be answered.

Mrs. Zuzana Mrázková works in her thesis on photovoltaic structures, respectively solar cells, incorporating crystalline and amorphous silicon (a:Si, partly with hydrogen added) as well as silicon nanowires (SiNW). Her thesis focuses on optical characterization, modeling, and design optimization of advanced solar cell architectures. These solar cells comprise inhomogeneous, i.e. deliberately textured samples, which enhance light-trapping and thus improve the solar cell performance, for photovoltaic applications. Optical measurements, mainly reflectometry, spectroscopic ellipsometry and Müller matrix polarimetry are used for fast and non-destructive characterization. All the techniques above (respectively the models describing it) rely on stratified layers; an assumption which is not fulfilled in the present case and the interpretation of the ellipsometric data becomes therefore more challenging. It is demonstrated that Zuzana was technically able and eager to use optical methods to study the widely used pyramidal textures as well as randomly oriented silicon nanowire arrays.

Chapter 1 discusses the photovoltaic market. Chapter 2 describes the sample preparation, i.e. the pyramidal textured c-Si template, on which the a:Si:H layers are grown, as well as SEM images of Sn- initiated SiNW growth. Chapter 3 explains the characterization methods, besides Ulbricht (integrating) sphere reflectometry, spectroscopic ellipsometry and angle resolved Müller matrix polarimetry. Chapter 4 outlines the theoretical background for optical modelling, chapter 5 discusses the results for pyramidal textured samples, chapter 6 for SiNWs. In addition I have to point out that my expertise is mainly in optics, and hardly in photovoltaics.

From the fundamental scientific point of view, however, there are- in my understanding - some omissions, which will be discussed below. From the experimental point of view, this thesis has been a very difficult and

very challenging one. I have to state in advance that some of my comments in the following will sound tough, strict and difficult. I hope to always address the basic physical understanding and the underlying models. **From an engineering perspective** (i.e. quality control, reproducibility and controllability) the designed optical model for calculation of the reflectance and absorption of thin film multi-layers on pyramidal surfaces is very good, as well as the first model fitting the experimental ellipsometric data for process control of plasma-assisted vapor-liquid-solid grown nanowires.

In order to understand my first set of comments (1-4) I will start with a discussion on homogeneous and inhomogeneous samples, and I expected a similar approach in chapter 4.

- 1) About Fresnel relations: Formally one can prove that the Fresnel relations are only correct for - and all derivations rely on- **homogeneous** samples. "Homogeneous" means that the wavelength of the probe (light) is much, much larger than the structure of the sample, or in other words ($d/\lambda \ll 1$). So, for stratified layers, as e.g. for layer L2 in Fig.6.5 the formulas for r_p, r_s are valid (despite atoms are inhomogeneous), and even if a thin "roughness layer" (L3) is on top, one can mathematically prove that under certain conditions the Fresnel relations describe the optical response correctly.
- 2) For **inhomogeneous** samples however, as presented in Fig. 6.12 a, with tin droplets, Fresnel fails, despite the ellipsometric angles ψ, Δ or 15 MM elements can still be measured. Then the question is, how to evaluate these data; as a "crude or rough" approximation one can still use a model relying on homogeneous assumption. If e.g. the distances between the single droplets is of the order of (a few times) the wavelength of light, (*and the same occurs with the facets in chapter 4*), then diffraction effects can be present. The data then evaluated are called **pseudo- dielectric function** denoted as $\langle \epsilon_r \rangle, \langle \epsilon_i \rangle$ or pseudo- refractive index $\langle n \rangle, \langle k \rangle$, and indicate that homogeneity is missing, (or there is a thin overlayer present, etc.) Figure 6.11, e.g. does not display the refractive index, but the pseudo- refractive index, and this distinction is important, as discussed in the next point:
- 3) By definition, there is only one refractive index (resp. one dielectric function) for one material, and this always indicates the bulk refractive index. If you structure such a material (i.e. the material is now inhomogeneous), e.g. a metal, lets say to 100 nm diameter cubes or spheres, the refractive index stays the same, but the optical response changes, due to diffraction effects. This is seldom taught, because the precise calculation of r_p, r_s now requires a **numerical** solution of Maxwell equations, which cannot any more be done with 3 plane waves (incoming, outgoing, transmitted), it needs infinitely many plane waves (then it is called RCWA) or a finite element solution (FEM). These are the only precise methods, even Rayleigh Rice approximations partly fail then. In these exact numerical calculations one still uses for Sn the tabulated **bulk dielectric function** (is still the same), but one puts voids (or air) in between and now solves the problem numerically. If it turns out, that for *all* your SE, MM measurements (i.e. for all azimuthal angles, and for all AOIs) the data are well described by using a **pseudo- dielectric**

function, then the quantity *"dielectric function of the given inhomogeneous structure"* can be well defined, otherwise one always has to get back to numerics.

So, Fig. 6.11 shows that the definition of a pseudo dielectric function is not a good approximation. But, because you measure in situ only with one angle, *only for this setup* using a pseudo-dielectric function can still describe the data well (compare e.g. Fig. 6.13). However, the physical interpretation has to be clear.

Zuzana, please make sure to distinguish between **dielectric function** and **pseudo- dielectric function in your final presentation**. (For your understanding, I attach to this email a recent paper (of my group), where this averaging procedure is described and additional effects are shown, too. (You can also google "spectroscopic ellipsometry and critical dimension analysis", to understand this procedure.)

- 4) (Only for completeness and understanding- not related to your thesis). The refractive index (not the pseudo!) as a physical property can change in addition, if there are quantization effects present, which modify the wave functions of the ground and excited states) : For semiconductors (at the band gap) this occurs for sizes $\leq 100nm$, for metals only for droplets $\leq 5nm$ (see Kreibig, Vollmer, *Optical Properties of Metal Clusters*).

I am now going through your thesis from the beginning and just list a few details, partly for didactic reasons and ask a few questions for better understanding (I am not an expert in photovoltaics):

- 5) Figure 2.2: please provide a height scale aside. As a side comment: you did a great job to reproducibly map SE and MM data for such corrugated structures, despite the underlying mathematics has not been correct.
- 6) Figure 2.3: where is the n-type layer?
- 7) Chapter 3.2.3 The angle resolved MM ellipsometry setup with a microscope objective is a fascinating tool!
- 8) Chapter 4.1.2. All the materials you work with are dispersive, because their dielectric functions depends on the frequency. $\varepsilon(\omega)$. Furthermore, writing $\varepsilon(\omega, \lambda)$ is misleading; either $\varepsilon(\omega)$ or $\varepsilon(\lambda_0)$ where λ_0 is denoting the vacuum wavelength.
- 9) Equ. 4.4a) is for not constant $\hat{\chi}_e$ wrong! The correct expression in real space is:

$$P_i(r, t) = \varepsilon_0 \int \chi_{ij}(r, r', t, t') E_j(r', t') dr dt = \varepsilon_0 \int \chi_{ij}(|r - r'|, |t - t'|) E_j(r', t') dr' dt'$$

where the homogeneity in time is always fulfilled, the homogeneity in space under the conditions discussed in comments (1-4) . Then, a convolution in time and space can be written as a product in Fourier space:

$$P_i(q, \omega) = \varepsilon_0 \chi_{ij}(q, \omega) E_j(q, \omega)$$

$$D_i(q, \omega) = \varepsilon_0 \varepsilon_{ij}(q, \omega) E_j(q, \omega) \dots \varepsilon_{ij} = \chi_{ij} + 1$$

And because the momentum of the photon is negligible against the one of the electron, the known

approximation results:

$$\begin{aligned} P_i(\omega) &= \varepsilon_0 \chi_{ij}(\omega) E_j(\omega) \\ D_i(\omega) &= \varepsilon_0 \varepsilon_{ij}(\omega) E_j(\omega) \end{aligned}$$

10) Chapter 4.2.1 on anisotropic samples: I do not agree on equ. 4.37, the more general form is published in the original work of Yeh (Surf. Sci 96, equ(4)). Equ. 4.37 is only correct, if one of the main axis of the dielectric tensor – after diagonalization is parallel to one axis of the lab coordinate system. Therefore I also doubt in eqs.(4.42); in my understanding this would indicate that incoming s- polarization always stays s- polarization, in any anisotropic material.

(Bye the way: where do you use anisotropic material properties in the Results section?)

- 11) From a didactic point of view, it would be better to present 4.2.3 before 4.2.1.
- 12) As already said in (1-4) your samples can hardly be described as “stratified layers”, so a discussion about RCWA (for periodic structures) or FEM would strongly show the complexity of the samples you investigated with SE and MM.
- 13) Concerning Figure 5.2: The drawing is 2-dimensional; does this -double reflection method - also work for 3D pyramids, especially close to the base of the pyramids. Can the number of reflections be computed with ray tracing simulations? The drawing is shown for normal incidence; aren't there critical angles where no second reflection occurs? How does the height distribution of the pyramids as well as the distance between two pyramids influence this concept?
- 14) Can the measured data in Figure 5.3 also be modelled if the angle of incidence is not normal?
- 15) Do I understand it correctly: Fig. 5.8 has been measured with normal incidence through a microscope lens and all 15 MM elements have been measured. What can be learned out of these 15 measurements?
- 16) I have difficulties to understand equ.(5.7): Is the absorption in the amorphous Si (a-Si:H) or a-SiC really parasitic? Does't this absorption generate carriers, which are separated and contribute to the total current?
- 17) Figure 5.19: if I understand Fig. 5.19 correctly, the grey area is the “useful one”, i.e. this is the absorption generating external current?
- 18) Concerning Figure 5.20: Can a flat, stratified, (i.e. no pyramidal texture) photovoltaic device be designed such that $J_{ph\ loss}$ is as small as a textured one? I.e: whatever layers are deposited on a flat device, $J_{ph\ loss}$ is larger than on a textured one?
- 19) My final comment for chapter 6: please distinguish between the **pseudo- dielectric function** (some people also call it “effective”) and the dielectric function.

Summing up all these comments as well as shown technical expertise and high experimental skills in this PhD thesis, it is clear that the thesis of the candidate Zuzana Mrazkova shall be defended.

With best regards

Kurt Hingerl

