Thin-film limit formalism applied to surface defect absorption

Jakub Holovský1,2* and Christophe Ballif3

1Institute of Physics of the Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Prague, Czech Republic
2CTU Faculty of Electrical Engineering, Technická 2, 166 27 Prague, Czech Republic
3École Polytechnique Fédérale de Lausanne (EPFL), Institute of Microengineering (IMT), Photovoltaics and Thin-Film Electronics Laboratory, Maladière 71, CH-2000 Neuchâtel, Switzerland

* jholovsky@gmail.com

Abstract: The thin-film limit is derived by a nonconventional approach and equations for transmittance, reflectance and absorptance are presented in highly versatile and accurate form. In the thin-film limit the optical properties do not depend on the absorption coefficient, thickness and refractive index individually, but only on their product. We show that this formalism is applicable to the problem of ultrathin defective layer e.g. on a top of a layer of amorphous silicon. We develop a new method of direct evaluation of the surface defective layer and the bulk defects. Applying this method to amorphous silicon on glass, we show that the surface defective layer differs from bulk amorphous silicon in terms of light soaking.

©2014 Optical Society of America

OCIS codes: (310.6860) Thin films, optical properties; (300.1030) Absorption.

References and links

1. Introduction

The so-called thin-film limit (TFL) or thin-film approximation is consistent with the concept of effective thickness that does not distinguish between thickness and absorption coefficient [1]. The thickness $d$ and dielectric function $\varepsilon$ of an atomic monolayer lose their usual physical meaning and are rather defined as tensors, related to each other as $\varepsilon = 1 - \frac{1}{\varepsilon_{\infty}}$. Similarly, Drude theory of inhomogenous ultrathin films predicts optical properties depending only on integral values of dielectric function over the film thickness [3]. Importantly, if the layer is parameterized by its absorption coefficient $\alpha$, thickness $d$ and refractive index $n$, the measurable optical properties $A$, $R$ and $T$ do not – in the FTL – depend on the parameters $\alpha$, $d$ or $n$ individually, but only on their product $\alpha d n$. Neither do they depend directly on the wavelength.

The derivation of the TFL is usually based on a linear approximation of the Fresnel equations in the limit of thickness going to zero [1,2,4–7]. These equations have appeared recently in a simple form for transmittance of freestanding graphene [6,8], but their general derivation also for reflectance is lacking in literature [7,9]. Here we show a new, simple and instructive derivation of these equations in an accurate and useful form that will be used to a new method of surface defect absorption, e.g. in hydrogenated amorphous silicon (a-Si:H).

Samples of a-Si:H are usually deposited as thin layers. Low absorptance measurements such as photothermal deflection spectroscopy (PDS) [10,11], constant photocurrent method (CPM) or Fourier-transform photocurrent spectroscopy [12,13] (FTPS) are used to evaluate defect absorption. Defect absorption may be elevated at the surfaces [11,14] enhancing interference pattern of absorptance (and hindering its smoothening by normalization by transmittance), depending on the side of illumination [15–17]. The evaluation of surface defect is complex and may be done either by varying sample thickness [11] or by comparison of absorptance measurements from layer and substrate side and complex simulations as done in our previous work [18]. However, under conditions of the TFL the defective layer can be parameterized only by only one “effective product” comprising of the product of its (virtual) thickness, refractive index and absorption coefficient. This significantly reduces the number of unknowns and the equations under TFL are also much simpler. Hence, the surface and bulk defects can be calculated directly without fitting.

2. Thin-film limit

We base our derivation on the conservation of energy, the continuity of the parallel components of an electric field across the layer and the assumptions of a low-absorbing medium ($n \gg k$) and a small thickness ($\alpha d \ll 1$, $dn \ll \lambda$). These approximations imply a linear dependence of the absorbed energy $I_A$ in a layer of an absorbing medium of thickness $d$,

$$I_A = I_{\text{eff}} \alpha d$$

(1)
where $I_{\text{eff}}$ is the “effective” energy flux. Note that the flux $I_{\text{eff}}$ is treated as a constant because Eq. (1) neglects its attenuation. The energy flux is related to its respective electric field through the time-averaged Poynting vector $S$, defined by Eq. (2).

$$I = \langle \mathbf{S} \rangle_{\text{time}} = \frac{1}{2} \sqrt{\frac{E_0}{\mu_0}} | \mathbf{E} |^2 n$$  \hspace{1cm} (2)

From this, it follows that also the effective electric field $E_{\text{eff}}$ is constant inside the layer. We define the measurable optical absorptance $A$ as $A = I_a/I_0$ by normalization to the energy flux of the incident wave $I_0$ propagating in the overlayer (refractive index $n_0$):

$$A \equiv \frac{I_a}{I_0} = \frac{|E_{\text{eff}}|^2}{|E_0|^2} \frac{\alpha dn}{n_0}$$  \hspace{1cm} (3)

To calculate the absorptance $A$, the value of $E_{\text{eff}}$ has to be known. In the same manner reflectance and transmittance are defined as $R = I_R/I_0$ and $T = I_T/I_0$. Employing the law of energy conservation $1 = A + R + T$ for the whole system, we can then write:

$$1 = \frac{|E_{\text{eff}}|^2}{|E_0|^2} \frac{\alpha dn}{n_0} + \frac{|E_R|^2}{|E_0|^2} + \frac{|E_T|^2}{|E_0|^2} n_2$$  \hspace{1cm} (4)

Again, based on our assumptions we neglect the evolution of the electric field throughout the ultrathin layer and assume the continuity of parallel components of electric fields:

$$E_n + E_n \equiv E_{\text{eff}} \equiv E_T$$  \hspace{1cm} (5)

This derivation does not rely on the electric field attenuation between two distinct borders of the thin film, but assumes only the presence of an “absorbing interface” where the value of the effective field $E_{\text{eff}}$ has to fulfill the conditions of Eqs. (4) and (5). Assuming $n \gg k$, it follows that the Fresnel coefficients $E_R/E_0$ and $E_T/E_0$ are real and the absolute-value brackets in Eq. (4) can be omitted. From Eqs. (4) and (5), we obtain a quadratic equation for $E_T/E_0$ featuring only one non-zero root, from which we obtain the transmittance $T_{\text{TFL}}$:

$$T_{\text{TFL}} = \frac{4n_0 n_2}{(n_0 + n_2 + \alpha dn)^2}$$  \hspace{1cm} (6)

Once $E_T$ is known, combining Eqs. (5) and (3), one obtains the absorptance $A_{\text{TFL}}$:

$$A_{\text{TFL}} = \frac{4 \alpha d n n_0}{(n_0 + n_2 + \alpha dn)^2}$$  \hspace{1cm} (7)

Reflectance then follows from energy conservation:

$$R_{\text{TFL}} = \frac{(n_0 - n_2 - \alpha dn)^2}{(n_0 + n_2 + \alpha dn)^2}$$  \hspace{1cm} (8)

To test of the TFL validity, especially in the case of graphene, is interesting as it points to the difficulty to directly measure its optical parameters. More detailed discussion as well as an experimental validation of the new TFL on graphene is published elsewhere [19].
4. Surface defect correction method

The surface defect correction method is based on the same set of approximations as the thin-film limit. The situation is sketched in Fig. 1. A layer with optical parameters, indexed by $a_1$, $d_1$, $n_1$, is deposited on glass with refractive index $n_2$. The ultrathin defective surface layer, labeled ‘01’, is described only by the effective product $(adn)_{01}$.

The absorptance in the defective layer can be calculated by Eq. (3) where we have to insert field $E_{\text{eff}}$ calculated by (5). We calculate $E_{\text{eff}}$ from reflected electric field for the top illumination and we calculate $E_{\text{eff}}$ from transmitted electric field for the bottom illumination. To distinguish between $E_{\text{eff}}$ for surface and interface -- will be discussed later -- we use labeling $E_{01}$ and $E_{12}$ respectively. When the layer is illuminated from top we use labeling “+”, conversely we use “-” for illumination from the substrate side. Assuming that the effect of the defective surface absorption has magnitude below 1% (usually it is much less) we can as well neglect the effect of the defective layer on the transmittance $t_{210}$ and reflectance $r_{210}$ of the whole stack. Symbols $r_{012}$ and $t_{210}$ indicate the amplitude (Fresnel) coefficients. The ascending order of the indices indicate the “+” direction of illumination and vice versa.

For the electric field at the interface $E_{01}$ we get

$$E_{01+} \equiv E_{0+} \left(1 + r_{02}\right)$$  \hspace{1cm} (10)

$$E_{01-} \equiv E_{2-} t_{210}$$  \hspace{1cm} (11)

where $E_{0+}$ and $E_{2-}$ are electric fields outside the stack, to which everything is normalized. By application of Eq. (3) we obtain $A_{01+}$ and $A_{01-}$, describing the absorptance of the interface layer for light incident from top and bottom respectively:

$$A_{01+} \equiv \left|1 + r_{02}\right|^2 \frac{(adn)_{01}}{n_0}$$  \hspace{1cm} (12)

$$A_{01-} \equiv \left|2 t_{02} \frac{(adn)_{01}}{n_2} \right|^2 = \left|\frac{n_2}{n_0} T_{02} \frac{(adn)_{01}}{n_0}\right|^2, \text{ where } T_{02} = \left|\frac{n_2}{n_0}\right|^2$$  \hspace{1cm} (13)

The total measured absorptances $A_{\text{tot}+}$ and $A_{\text{tot}-}$ include both the absorptances of the bulk layer and the surface defective layer. The back reflectance $R_{02} = (n_0 - n_2)^2 / (n_0 + n_2)^2$ of the back side of the substrate is also taken into account:

$$A_{\text{tot}+} \equiv A_{0+} + A_{01+} + \frac{T_{012} R_{02}}{1 - R_{02} T_{210}^2} \left(A_{+} + A_{01-}\right)$$  \hspace{1cm} (14)

$$A_{\text{tot}-} \equiv \frac{1 - R_{02}}{1 - R_{02} T_{210}^2} \left(A_{-} + A_{01-}\right)$$  \hspace{1cm} (15)

In the low and medium absorption region, we can, assuming $k^2 / n^2 \ll 1$ and $1 - e^{-ad} = ad$, use Eq. (4) from Ritter and Weiser [20], to calculate:

---

Fig. 1. Sample of layer with surface defective layer at the top surface or at the interface with substrate.

---
\[ A_i \, / \, A_r = (n_r^2 n_i^2 + n_i^2 n_r^2) / (n_r^2 n_i^2 + n_i^2 n_r^2) \equiv b \quad (16) \]

Then, if we calculate the difference \( A_{tot+} \) and \( cA_{tot-} \), where \( c \) fulfills equation

\[ b \left( 1 - R_{02} \right) \overline{210}^2 + T_{012} R_{02} - c (1 - R_{02}) = 0, \quad (17) \]

we obtain simple relation:

\[ A_{tot+} - cA_{tot-} \equiv A_{01+} - bA_{01-}. \quad (18) \]

Using Eqs. (12) and (13) we can access the effective product \((\alpha d_n)_{01}\) as follows:

\[ A_{tot+} - cA_{tot-} = (\alpha d_n)_{01} \left( \frac{1}{n_0 |l + r_{012}|^2} - b \frac{n_r^2}{n_i^2} |p_{012}|^2 \right) \quad (19) \]

where \( r_{012} = r_{10} + r_{12} e^{2i\beta} \), \( r_{012} = \frac{t_{01} t_{12} e^{i\beta}}{1 - r_{01} r_{12} e^{2i\beta}} \), \( \beta = 2\pi N_i d / \lambda \), \( N_i = n_i + \alpha_i \lambda / 4\pi \) and \( t_{01}, r_{ij} \)

are intensity Fresnel coefficients for perpendicular incidence on \( i/j \) interface. Once knowing \((\alpha d_n)_{01}\), we can get to \( A_{01-} \) from Eq. (13) and to \( A_{1-} \) from Eq. (15):

\[ A_{1-} = A_{tot-} \left( 1 - \frac{R_{02} \overline{210}^2}{1 - R_{02}} \right) \frac{(\alpha d_n)_{01}}{n_0} \quad (20) \]

The absorptance in bulk \( A_{1-} \) divided by transmittance (an interference-free quantity), can be used to calculate the absorption coefficient \( \alpha_1 \) by Eq. (6) in [20]. The evaluation is two-step: Standard evaluation [20,21] gives \( \alpha_1 \) \((n_1) \) is simulated by Cauchy formula) in high absorption region, neglecting surface defects; then \( \alpha_1 \) \( n_1 \) are inserted into \( c \) and the right side of Eq. (19).

4. Interface defects correction method

In [18] we have shown that, if the defect density is both at top surface and at the interface with substrate, the surface correction is practically impossible. However, when the defective layer is only at the interface (labeled “12”), represented by effective product \((\alpha d_n)_{12}\), the Eqs. (21), (22) analogous to (19), (20) can be derived:

\[ A_{tot+} - cA_{tot-} = (\alpha d_n)_{12} \left( \frac{1}{n_0 |l + r_{012}|^2} - b \frac{n_r^2}{n_i^2} |p_{012}|^2 \right) \quad (21) \]

\[ A_{1-} = A_{tot-} \left( 1 - \frac{R_{02} \overline{210}^2}{1 - R_{02}} \right) - |l + r_{012}| \frac{c (\alpha d_n)_{12}}{n_2} \quad (22) \]

Note that the Eqs. (16), (17), (19)-(22) simplify when the substrate back surface can be neglected \((R_{02} = 0)\). This is the case of PDS where refractive index of ambient is close to 1.5.
4. Results and discussion

We simulated the complete situation by the transfer-matrix method [22]. We first defined the structure as in the Fig. 1 with $d_1 = 360\text{nm}$, $n_1 = n_{a-\text{Si:H}}$, the thickness of the defective layer was 3nm and its refractive index was the same as the layer. We calculated $A_{\text{tot}+}$, $A_{\text{tot}–}$ and $T$ by transfer matrix method. Then we extracted back the absorption of bulk $A_1–$ and $A_1+$ and surface effective products $(a dn)_{01}$ and $(a dn)_{12}$ by Eqs. (19)-(22), see Fig. 2.

The accuracy and robustness of the calculation depends on how far from zero are the values on left and right side of the Eq. (19) and (21). This depends on the refractive index $n_2$: When we are in the region of low absorptance and if $n_2 = n_1$ then, every time the $T$ is in maximum, right sides of (19) and (21) go to zero, which is a singularity in the calculation. On the other hand, when $n_2 > n_1$ no singularity occurs in the right side of (19) whereas the right side of (21) has even more singularities because it crosses zero many times. That is why the correction performs better for defective surface than defective interface, as we see in Fig. 2.

We applied the correction method to the experiment described in [18], where we had identified defective layer on the top surface. A 360 nm thick hydrogenated amorphous silicon was deposited on glass by plasma-enhanced chemical vapor deposition. The spectra of $A_{\text{tot}+}$, $A_{\text{tot}–}$ and $T$ were measured by FTPS and PDS. The measurements were repeated in time and as the last step, the sample was light soaked. A significant evolution was observed in the curves around energy 1.2 eV where absorptance corresponds to defect density [12,21,23], see Fig. 3. The $A_{\text{tot}–}$ curves were multiplied by $c$ and all curves were put into absolute scale to fit to PDS results at region around 1.7eV (FTPS is not an absolute method). This gave the left side of the Eq. (19) and $(a dn)_{01}$ was calculated. From Eq. (20) $A_1–$ was obtained and absorption coefficient $\alpha_1$ was calculated by [20] and bulk defect states assessed by [23] assuming density of atoms in bulk $\sim 4\times 10^{22}\text{cm}^{-2}$. Surface defects were calculated by dividing $(a dn)_{01}$ by refractive index of bulk ($n_1 \sim 3.5$) and assuming density of surface atoms $\sim 10^{15}\text{cm}^{-2}$. We can observe similar trend of decrease of bulk and surface states in time. After the light soaking step bulk defect density increases significantly whereas the surface defects keep decreasing.
4. Conclusion

Together with a new way of thin-film limit derivation we developed a simple and direct method of evaluation of defective layer at surface of thin layer or at interface of the layer with substrate. This method compares absorption measurement from layer side and glass side and works well if only one (either at the surface or at the interface with glass) defective layer thinner than 3nm is present. Separate evaluation of surface and bulk defect states is crucial. Here it helped to reveal different behavior of bulk and surface during light soaking.

Acknowledgment

We acknowledge support of 7th EU framework “Fast-Track” project no 283501 supplemented by support of Czech ministry of education no 7E12029 and Czech Science Foundation grant GA14-05053S. We thank Michael Stückelberger for sample preparations.