Thin-film limit formalism applied to surface defect absorption

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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.

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

References and links

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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 ε of an atomic monolayer lose their usual physical meaning and are rather defined as tensors, related to each other as $(\vec{\varepsilon}-1)\cdot\vec{d}=4\pi N\vec{\rho}$, where N and $\vec{\rho}$ is the density of dipoles and the vector of polarizability [2]. 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 α, thickness d and refractive index n, the measurable optical properties A, R and T do not – in the FTL – depend on the parameters α, d or n individually, but only on their product αdn. 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,

$$I_A \approx I_{\text{eff}}\alpha d\,, \tag{1}$$

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where I_{eff} is the "effective" energy flux. Note that the flux I_{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).

$$I = \langle S \rangle_{\text{time}} = \frac{1}{2}\sqrt{\frac{\varepsilon_0}{\mu_0}}\,|E|^2\, n \tag{2}$$

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

$$A \equiv \frac{I_A}{I_0} = \frac{|E_{\text{eff}}|^2\,\alpha d n}{|E_0|^2\, n_0} \tag{3}$$

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

$$1 = \frac{|E_{\text{eff}}|^2}{|E_0|^2}\frac{\alpha d n}{n_0} + \frac{|E_{\text{R}}|^2}{|E_0|^2} + \frac{|E_{\text{T}}|^2}{|E_0|^2}\frac{n_2}{n_0} \tag{4}$$

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:

$$E_0 + E_{\text{R}} \cong E_{\text{eff}} \cong E_{\text{T}} \tag{5}$$

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_{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_{TFL}:

$$T_{\text{TFL}} = \frac{4 n_0 n_2}{\left(n_0 + n_2 + \alpha d n\right)^2} \tag{6}$$

Once E_{T} is known, combining Eqs. (5) and (3), one obtains the absorptance A_{TFL}:

$$A_{\text{TFL}} = \frac{4 \alpha d n n_0}{\left(n_0 + n_2 + \alpha d n\right)^2} \tag{7}$$

Reflectance then follows from energy conservation:

$$R_{\text{TFL}} = \frac{\left(n_0 - n_2 - \alpha d n\right)^2}{\left(n_0 + n_2 + \alpha d n\right)^2} \tag{8}$$

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].

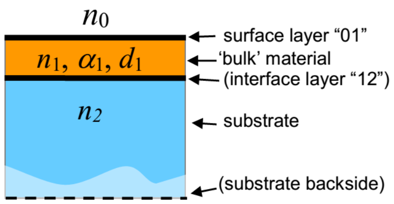

Fig. 1. **S**ample of layer with surface defective layer at the top surface or at the interface with substrate.

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 α_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 value of the effective product $(\alpha dn)_{01}$.

The absorptance in the defective layer can be calculated by Eq. (3) where we have to insert field E_{eff} calculated by (5). We calculate E_{eff} from reflected electric field for the top illumination and we calculate E_{eff} from transmitted electric filed for the bottom illumination. To distinguish between E_{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 t_{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

$$E_{01+} \cong E_{0+}\left(1+r_{012}\right) \tag{10}$$

$$E_{01-} \cong E_{2-}\ t_{210}\ , \tag{11}$$

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:

$$A_{01+} \cong \left|1+r_{012}\right|^2 \frac{(\alpha dn)_{01}}{n_0} \tag{12}$$

$$A_{01-} \cong \left|t_{210}\right|^2 \frac{(\alpha dn)_{01}}{n_2} = \left|t_{012}\right|^2 \frac{n_2}{n_0^2}(\alpha dn)_{01} = T_{012}\frac{(\alpha dn)_{01}}{n_0}, \quad \text{where} \quad T_{012} = \left|t_{012}\right|^2 \frac{n_2}{n_0} \tag{13}$$

The total measured absorptances $A_{\mathrm{tot}+}$ and $A_{\mathrm{tot}-}$ 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:

$$A_{tot+} \cong A_{1+} + A_{01+} + \frac{T_{012}R_{02}}{1-R_{02}\left|r_{210}\right|^2}\left(A_{1-} + A_{01-}\right) \tag{14}$$

$$A_{tot-} \cong \frac{1-R_{02}}{1-R_{02}\left|r_{210}\right|^2}\left(A_{1-} + A_{01-}\right) \tag{15}$$

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

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$$A_{1+}/A_{1-} \cong (n_0 n_1^2 + n_0 n_2^2)/(n_1^2 n_2 + n_0^2 n_2) \equiv b \tag{16}$$

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

$$b\left(1 - R_{02}\left|r_{210}\right|^2\right) + T_{012}R_{02} - c\left(1 - R_{02}\right) = 0, \tag{17}$$

we obtain simple relation:

$$A_{\mathrm{tot}+} - cA_{\mathrm{tot}-} \cong A_{01+} - bA_{01-} \tag{18}$$

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

$$A_{\mathrm{tot}+} - cA_{\mathrm{tot}-} \cong (\alpha dn)_{01}\left(\frac{1}{n_0}\left|1 + r_{012}\right|^2 - b\frac{n_2}{n_0^2}\left|t_{012}\right|^2\right), \tag{19}$$

where $r_{012} = \dfrac{r_{01} + r_{12}e^{2i\beta}}{1 - r_{10}r_{12}e^{2i\beta}}$, $t_{012} = \dfrac{t_{01}t_{12}e^{i\beta}}{1 - r_{10}r_{12}e^{2i\beta}}$, $\beta = 2\pi N_1 d/\lambda$, $N_1 = n_1 + \alpha_1\lambda/4\pi$ and t_{ij}, r_{ij} are intensity Fresnel coefficients for perpendicular incidence on i/j interface. Once knowing $(\alpha dn)_{01}$, we can get to A_{01-} from Eq. (13) and to A_{1-} from Eq. (15):

$$A_{1-} \approx A_{tot-}\frac{1 - R_{02}\left|r_{210}\right|^2}{1 - R_{02}} - T_{012}\frac{(\alpha dn)_{01}}{n_0} \tag{20}$$

The absorptance in bulk A_{1-} divided by transmittance (an interference-free quantity), can be used to calculate the absorption coefficient α_1 by Eq. (6) in [20]. The evaluation is two-step: Standard evaluation [20,21] gives α_1 (n_1 is simulated by Cauchy formula) in high absorption region, neglecting surface defects; then α_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 $(\alpha dn)_{12}$, the Eqs. (21), (22) analogical to (19), (20) can be derived:

$$A_{\mathrm{tot}+} - cA_{\mathrm{tot}-} \cong (\alpha dn)_{12}\left(\frac{1}{n_0}\left|t_{012}\right|^2 - \frac{b}{n_2}\left|1 + r_{210}\right|^2\right) \quad \text{, where } \; r_{210} = \frac{r_{21} + r_{10}e^{2i\beta}}{1 - r_{10}r_{12}e^{2i\beta}} \tag{21}$$

$$A_{1-} \approx A_{tot-}\frac{1 - R_{02}\left|r_{210}\right|^2}{1 - R_{02}} - \left|1 + r_{210}\right|^2\frac{(\alpha dn)_{12}}{n_2} \tag{22}$$

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.

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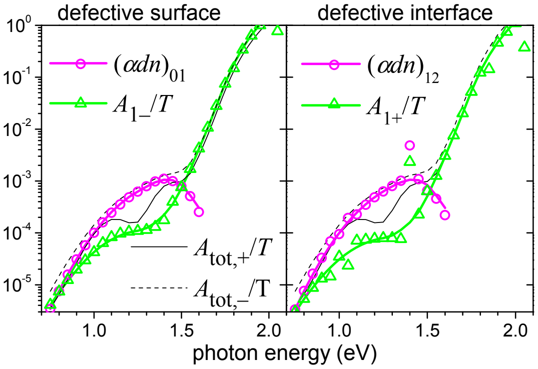

Fig. 2. Absorption in bulk material – represented by A_1/T ratio, and in 3nm thick defective layer – represented by $(\alpha dn)_{ij}$, either or on surface or on glass-layer interface. Lines are directly simulated, symbols are extracted by the correction method presented here from rigorously simulated data of $A_{\mathrm{tot}+}/T$, $A_{\mathrm{tot}-}/T$ (thin black lines).

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 = 360nm, $n_1 = n_{\text{a-Si:H}}$, the thickness of the defective layer was 3nm and its refractive index was the same as the layer. We calculated $A_{\mathrm{tot}+}$, $A_{\mathrm{tot}-}$ and T by transfer matrix method. Then we extracted back the absorption of bulk A_{1-} and A_{1+} and surface effective products $(\alpha dn)_{01}$ and $(\alpha dn)_{12}$ 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 $A_{\mathrm{tot}+}$, $A_{\mathrm{tot}-}$ 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 $A_{\mathrm{tot}-}$ 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 $(\alpha dn)_{01}$ was calculated. From Eq. (20) A_{1-} was obtained and absorption coefficient α_1 was calculated by [20] and bulk defect states assessed by [23] assuming density of atoms in bulk ~$4\times10^{22}\mathrm{cm}^{-2}$. Surface defects were calculated by dividing $(\alpha dn)_{01}$ by refractive index of bulk (n_1~3.5) and assuming density of surface atoms ~$10^{15}\mathrm{cm}^{-2}$. 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.

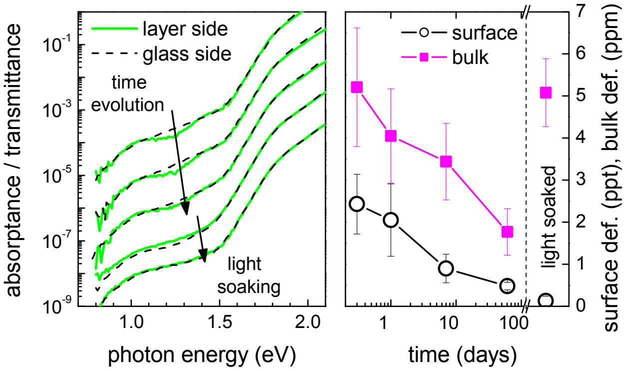

Fig. 3. Left part – FTPS spectra, measured from layer side and glass side, divided by transmittance, multiplied by *c*. Lower curves are consecutively shifted by a factor 1/10 form the one on top. Right part – surface defects in part per thousand of surface atoms and bulk defects in part per million of bulk atoms, extracted by our method.

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.

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