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# Application of sum rule to the dispersion model of hydrogenated amorphous silicon

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ABSTRACT

Optical data obtained for a-Si:H films by ellipsometry and spectrophotometry in the wide photon energy range 0.046–8.9 eV are fitted using the analytical dispersion models based on the application of the sum rule. The models include all absorption processes ranging from phonon absorption in IR region to core electron excitations in X-ray region. They take into account the existence of extended and localized states of valence electrons and distinguish transitions to conduction band and higher energy electron states. It is demonstrated that a combination of optical measurements over the wide range, combined with reasonable assumptions about the optical response in regions where no experimental data are available can lead to dispersion models enabling to determine the mass density of the film. Comparing the density of states determined by tight-binding method with that obtained from optical data, it is shown that an excitonic effect is significant in a-Si:H and causes a redistribution of transition probability from higher energies to the broad peak centered at 3.5 eV. Moreover, it is suggested how to apply the sum rule in the commercial ellipsometric software implementing the Tauc–Lorentz model.

## 1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is a material of strategic importance in microelectronics and solar cell applications [1]. Its electronic and optical properties are significantly influenced by the degree of disorder and hydrogen concentration [2] and therefore optical methods such as spectrophotometry and ellipsometry are commonly used for a-Si:H characterization [3–8]. The analysis of the optical data requires a suitable dispersion model. Several analytical formulas describing the dielectric response of a-Si:H, i.e. complex dielectric function or optical constants, have been published [3–5,9]. These models are based on various modifications of the classical damped harmonic (Lorentz) oscillator model. All these models can be used only in a restricted spectral range because they take into account only the interband transitions. In particular the Tauc–Lorentz (TL) dispersion model [4] has become popular in the last decade because it describes the dielectric response of the amorphous materials quite well and it can be easily implemented.

The theory of dispersion implies the three general conditions for the dielectric function: the Kramers–Kronig (KK) relation following from causality [10–12]; the time-reversal symmetry that holds because the response function is real [12] and the *f*-sum rule that connects the dielectric function to the density of charged particles and follows from the laws of motion [12–15]. Although these conditions have been well-known for a long time not all dispersion models used in practice satisfy them. For instance the Forouhi–Bloomer model [9] satisfies neither the time-reversal symmetry nor *f*-sum rule.

In classical textbooks, the *f*-sum rule is derived under the assumption that dielectric response of solids is only given by the response of electrons [12–15]. In our recent paper [16] the sum rule was generalized on the basis of the Thomas–Reiche–Kuhn sum rule [17–19] applied to electrons and nuclei in the following form:

$$\int_0^\infty \mathcal{F}(E)\mathrm{d}E = \mathcal{N}_\mathrm{e} + \sum_n \frac{Z_n^2 m_\mathrm{e}}{m_n}\mathcal{N}_n = \mathcal{U}\mathcal{N}_\mathrm{e}, \tag{1}$$

where the summation is performed over all types of nuclei $n$ within the system. The symbols $Z_n$, $m_\mathrm{e}$, $m_n$, $\mathcal{N}_\mathrm{e}$ and $\mathcal{N}_n$ denote the proton number, mass of electron, mass of nuclei density of electrons and density of nuclei, respectively. The factor $\mathcal{U}$ is practically identical for most materials: $\mathcal{U} \approx 1.00027$ [16]. Function $\mathcal{F}(E)$, called *transition strength function*, is a continuous condensed-matter equivalent of the oscillator strength known for discrete transitions in atomic spectra. For parametrization of dielectric function in frame of dipole approximation it is practical to introduce the function $F(E) = \varepsilon_\mathrm{i}(E)E \approx \mathcal{F}(E)/\mathcal{M}$, where $\mathcal{M} = 8\pi\epsilon_0 m_\mathrm{e}/(eh)^2$. This function can also be called transition strength function and serves as a starting point for the parametrization of optical constants of solids in general.

In this paper the dispersion model of a-Si:H based on parametrization of $F(E)$ and application of the sum rule will be presented. Theoretical background is discussed in details in our previous paper [16].

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## 2. Parametrization of dielectric response

The transition strength function $F(E)$ is composed from individual contributions indexed by $t$ belonging to individual absorption effects:

$$F(E)=\sum_t F_t(E). \tag{2}$$

It is practical to introduce the normalized transition strength functions $F_t^0(E)$ and normalized dielectric functions $\varepsilon_t^0(E)$ in the following way:

$$F_t(E)=N_t F_t^0(E), \qquad \int_0^\infty F_t^0(E)\mathrm{d}E=1, \tag{3}$$

$$\varepsilon(E)=1+\sum_t N_t\varepsilon_t^0(E), \tag{4}$$

where $N_t$ is transition strength of the individual contribution $t$. The sum of all $N_t$ is called *total transition strength*:

$$\sum_t N_t=N \tag{5}$$

and it is equal to the right hand side of sum rule (1) divided by $\mathcal{M}$ (more details in Section 2.8).

The real and imaginary parts of normalized dielectric functions are then determined from normalized strength functions as follows

$$\varepsilon_{\mathrm{r},t}^0(E)=\frac{2}{\pi}\fint_0^\infty \frac{F_t^0(X)}{X^2-E^2}\mathrm{d}X, \quad \varepsilon_{\mathrm{i},t}^0(E)=\frac{F_t^0(E)}{E}, \tag{6}$$

where the first formula in (6) follows from KK relation and time-reversal symmetry and the second formula is given by the definition of $F(E)$.

In a-Si:H the absorption is caused by the following effects corresponding to the individual contributions $t$ in transition strength function:

- **vc** Electron interband transitions from valence to conduction band, i.e. $\sigma\rightarrow\sigma^*$ (absorption on extended states).
- **vx** Excitation of electrons from the valence band to the band corresponding to higher energy electron states above the conduction band, i.e. $\sigma\rightarrow\xi^*$.
- **u** Transitions from valence band to empty localized states and from occupied localized states to conduction band, i.e. $\sigma\rightarrow\lambda^*$ and $\lambda\rightarrow\sigma^*$ (Urbach tail).
- **K**, **L** Excitation of electrons from the core levels to the electron states above Fermi energy, i.e. to conduction and higher energy bands, $K+L\rightarrow\sigma^*+\xi^*$.
- **ph** Phonon absorption, i.e. excitation of vibrational states of nuclei.
- **loc** Transitions on localized states, i.e. $\lambda\rightarrow\lambda^*$.

The first four contributions can be expressed within the one-electron approximation as transitions between occupied and empty bands [16] that are schematically depicted in Fig. 1. The parametrization of the individual contributions is presented in the following subsections.

### 2.1. Valence-to-conduction interband transitions

In amorphous materials with one valence and one conduction band the contribution of interband transitions is non-zero for energies from $E_\mathrm{g}$ to $E_\mathrm{h}$, where parameter $E_\mathrm{g}$ is the band gap and parameter $E_\mathrm{h}$ is the upper energy limit of transitions (see Fig. 1). The $\mathcal{J}(E)$ joint density of states (JDOS) is quadratic in vicinity of these energy limits [16,20] and for asymmetric form of JDOS the following formula for interband transitions is suitable

$$\varepsilon_{\mathrm{i,vc}}^0(E)=\mathrm{sgn}(E)\frac{\left(|E|-E_\mathrm{g}\right)^2(E_\mathrm{h}-|E|)^2}{\mathcal{C}_\mathrm{N}E^2\left[(|E|-E_\mathrm{c})^2+B_\mathrm{c}^2\right]}\Pi_{E_\mathrm{g},E_\mathrm{h}}(|E|), \tag{7}$$

where the Lorentzian factor in denominator with parameters $E_\mathrm{c}$ and $B_\mathrm{c}$ influences the asymmetry and the broadness of $\varepsilon_{\mathrm{i,vc}}^0$. The symbol $\Pi_{E_\mathrm{g},E_\mathrm{h}}$ denotes the step-like function defined as follows:

$$\Pi_{E_\mathrm{min},E_\mathrm{max}}(E)=\begin{cases}1 & : \quad E_\mathrm{min}<E<E_\mathrm{max}\\ 0 & : \quad \text{otherwise.}\end{cases} \tag{8}$$

The real part of normalized dielectric function obtained using Kramers–Kronig relation (6) and normalization factor $\mathcal{C}_\mathrm{N}$ obtained using (3) are presented in Appendix A.

### 2.2. High energy valence electron excitations

The transitions from the valence band to the higher energy electron states are described using a two-parameter model presented in [16]:

$$\varepsilon_{\mathrm{i,vx}}^0(E)=\frac{F_\mathrm{vx}^0(E)}{E}=\frac{3E_\xi\left(|E|-E_\xi\right)^2}{E^5}\Pi_{E_\xi,\infty}(|E|), \tag{9}$$

where $E_\xi=E_g/2+E_x$ is the minimum energy of the transitions (see Fig. 1). According to (6), the real part of $\varepsilon_\mathrm{vx}^0(E)$ is given as

$$\varepsilon_{\mathrm{r,vx}}^0(E)=\frac{3E_\xi}{\pi E^2}\left[a(E)\ln\left|1-\frac{E}{E_\xi}\right|+b(E)\ln\left|1+\frac{E}{E_\xi}\right|-\frac{2}{3E_\xi}-\frac{2E_\xi}{E^2}\right], \tag{10}$$

where

$$a(E)=-\frac{\left(E_\xi-E\right)^2}{E^3}, \quad b(E)=\frac{\left(E_\xi+E\right)^2}{E^3}. \tag{11}$$

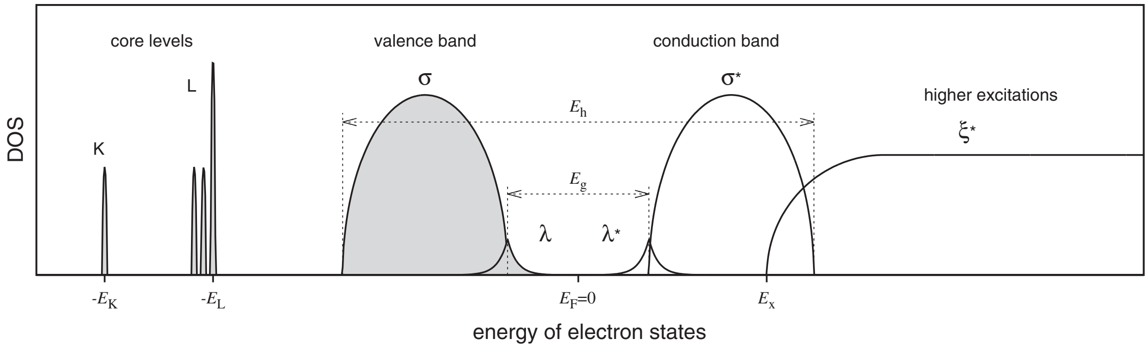

**Fig. 1.** Schematic diagram of density of states (DOS) of a-Si:H. Occupied states below the Fermi energy $E_F$ are depicted by the shaded area.