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Parameterization of the dielectric function of semiconductor nanocrystals

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ABSTRACT

Optical methods like spectroscopic ellipsometry are sensitive to the structural properties of semiconductor films such as crystallinity or grain size. The imaginary part of the dielectric function is proportional to the joint density of electronic states. Consequently, the analysis of the dielectric function around the critical point energies provides useful information about the electron band structure and all related parameters like the grain structure, band gap, temperature, composition, phase structure, and carrier mobility. In this work an attempt is made to present a selection of the approaches to parameterize and analyze the dielectric function of semiconductors, as well as some applications.

1. Introduction

Optical methods, especially polarimetric techniques like ellipsometry, are capable of measuring the structural properties of semiconductors [1,2]. Ellipsometry (and most reflection-based optical methods) can measure nanocrystals in thin layers of optical quality having interfaces that are planar on the scale of several nanometers. The electronic structure of crystalline semiconductors changes strongly with the variation of long range order in the crystal lattice. The imaginary part of the dielectric function measured by ellipsometry is related to the electronic structure (joint density of states), and it is largely influenced by crystallinity around the critical point energies corresponding to transition energies between parallel bands of the Brillouin zone, revealing high absorption. There is a broad range of material properties that can be determined based on the analysis of the dielectric function, as shown in Fig. 1 [3].

Characteristic critical point energies are 3.4 and 4.2 eV in Si. A spectral range covering these photon energies can easily be measured by standard ellipsometric hardware, usually including the photon energy range of 1.5–5.0 eV and being capable of acquiring accurate and reliable spectra. While the dielectric functions of most single-crystalline semiconductors are available in the literature, the largest problem of measuring non-single-crystalline semiconductors is the requirement of appropriately modeling the dielectric function. There have been numerous approaches like effective medium or oscillator models investigated in the literature used in versatile applications from polycrystalline thin films [4] through ion implanted semiconductors [5,6] to porous or nanocrystalline structures [7–10]. There is a trade off between the robustness and the number of fitted parameters used in the optical models. Oscillator models are more accurate, but the large number of fit parameters requires experience, a systematic fitting approach or sophisticated parameter search procedures to avoid getting in local minima.

Another source of error is a possible lateral and vertical inhomogeneity of thin films, which are not taken into account in first order. The most general problem is the vertical non-uniformity, which is a characteristic of most deposited thin films. It does not only mean a surface and interface roughness or an interface layer of nucleation, but in some cases also a gradual change of properties in the vertical direction, as in most polycrystalline films [11,12]. A depth scan can be performed by fitting in different wavelength ranges (e.g. for Si the smallest wavelength is fixed at the position for the largest absorption, and the longest wavelength of the range is gradually increased to increase the penetration depth), utilizing the fact that the optical penetration depth changes to a great extent as a function of wavelength around the critical point energies [13].

2. Effective medium methods

Effective medium methods are the most widely used and robust ways to describe the dielectric function of not only semiconductors but any other composite structures consisting of distinct phases that can be described by their bulk dielectric functions and that are smaller than the wavelength of illumination

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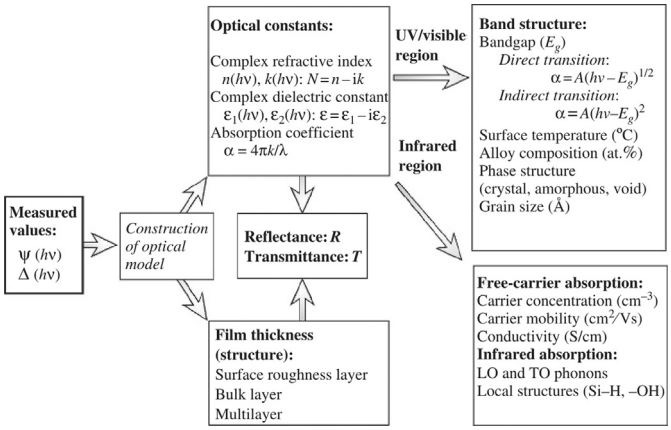

Fig. 1. Scheme of an ellipsometric measurement. Optical models are constructed to determine optical properties and layer thicknesses. The reflectance and transmittance are not measured directly, but they can be determined from the optical models using the best-fit parameters. There is a large number of material properties that can be determined from the optical properties. Due to the high sensitivity of ellipsometry to the dielectric function (10^{-3}–10^{-4}), material properties with small influence on the optical properties can also be measured. (Reproduced from Ref. [3].)

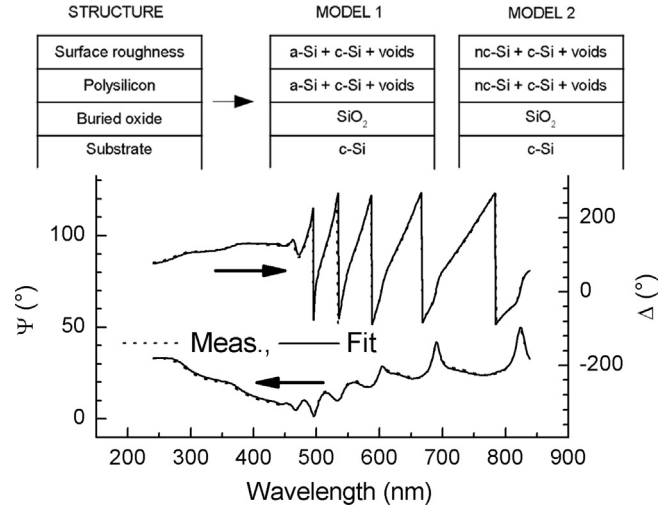

Fig. 2. Measured (angle of incidence of 75°) and fitted ellipsometric spectra of a 100-nm polycrystalline Si film deposited on oxidized (100 nm) Si using low pressure chemical vapor deposition at a temperature of 640 °C. At the top of the figure the assumed layer structure and two possible optical models depending on the grain structure are shown. In this fit Model 2 has been used.

[4,14]. The effective dielectric function (ϵ) can be calculated from the dielectric functions of the components ($\epsilon_a, \epsilon_b, \ldots$) and their volume fractions ($f_a, f_b, \ldots$) by the equation

$$\frac{\epsilon-\epsilon_h}{\epsilon+2\epsilon_h}=f_a\frac{\epsilon_a-\epsilon_h}{\epsilon_a+2\epsilon_h}+f_b\frac{\epsilon_b-\epsilon_h}{\epsilon_b+2\epsilon_h}, \tag{1}$$

where ϵ_h denotes the dielectric function of the host. If ϵ_b represents a dilute phase, then we can choose $\epsilon_h=\epsilon_a$, which leads to the Maxwell Garnett expression:

$$\frac{\epsilon-\epsilon_a}{\epsilon+2\epsilon_a}=f_b\frac{\epsilon_b-\epsilon_a}{\epsilon_b+2\epsilon_a}. \tag{2}$$

If the volume fractions of the components are comparable, it may not be clear which component would be the host medium. In this case a self-consistent choice is $\epsilon_h=\epsilon$ resulting in the Bruggeman expression:

$$0=f_a\frac{\epsilon_a-\epsilon}{\epsilon_a+2\epsilon}+f_b\frac{\epsilon_b-\epsilon}{\epsilon_b+2\epsilon}. \tag{3}$$

A typical example of the Bruggeman effective medium theory is the modeling of polycrystalline materials, which can usually be considered as a composition of certain phases like single-crystalline Si (c-Si), amorphous Si (a-Si), fine-grained polycrystalline Si (nc-Si) and voids (vacuum, i.e. a refractive index of $n=1$) for polycrystalline Si [15,11,16], as shown in Fig. 2.

3. Analytical models

If the assumption that the investigated film has distinct phases is not valid, or if there is no reliable reference dielectric function for the components, the effective medium approach fails. Analytical models describe the dielectric function with parameterized functions derived from physical principles like the generalized oscillator model [17], the model dielectric function [18] or the Forouhi–Bloomer model [19], or providing mathematical line shapes such as the Kim–Garland model [20], the Johs–Herzinger model [21] or the B-spline model [22]. While the advantage of the effective medium models is that they describe the optical properties with few parameters and that they allow the determination of volume fractions of known phases, the major advantage of analytical parameterizations is that their fitted parameters can be related to numerous derived physical properties that are highly relevant in semiconductor technology and materials science (see Fig. 1).

3.1. Lorentz oscillators

A general and usual approach to fit the dielectric function is to use a set of Lorentz oscillators:

$$\epsilon_L(E)=\epsilon_{L,\infty}+\sum_{i=1}^{n}\frac{A_{i,L}^2}{(E_{i,L}^2-E^2)-i\Gamma_{iL},E}, \tag{4}$$

where E, A_L, Γ_L and E_L denote the photon energy, the amplitude, the broadening and the oscillator energy, respectively. This method is often used to have a smooth analytical representation of the dielectric function which allows the accurate determination of peak positions and broadenings [23] or serves as a starting point for further analysis [24]. This method has been extended with Gaussian broadening to achieve a better fit on metal films [25]. It has been shown by numerous investigations that the broadening parameter of the critical point features is proportional to the grain size [24,9].

If the size of nanocrystal inclusions is so small that the band structure gets close to that of amorphous semiconductors, then the Tauc–Lorentz method can be applied [26,27]. This approach combines (i.e. calculates the convolution of) Lorentz oscillators and the quadratic Tauc gap

$$\epsilon_{2,T}(E)=\frac{A_T E_{0,T}\Gamma_T(E-E_{g,T})^2}{(E^2-E_{g,T}^2)^2+\Gamma_T^2E^2}\Theta(E-E_{g,T}), \tag{5}$$

where $\Theta(x<0)=0$, $\Theta(x\geq 0)=1$, A_T, Γ_T, $E_{g,T}$ and $E_{0,T}$ are the amplitude, the broadening, the band gap and the peak energy in the joint density of states, respectively. The corrected expression for the real part of the dielectric function is given in Ref. [28]. The Tauc–Lorentz method has been proven to be useful for modeling amorphous semiconductors. This way a quadratic behavior is assumed at the band edge while the simplicity of the combination of Lorentz oscillators is maintained. In the model a Kramers–Kronig consistent analytical formula is constructed for the real part of the dielectric function. This provides simplicity for the computational adaptation of the model, and at the same time provides a powerful concept, because well-defined numerical information (like the band gap) can be determined for the