
Characterization of Nanocrystals Using Spectroscopic Ellipsometry

Peter Petrik

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1. Introduction

First applications of ellipsometry to the measurement of poly- and nanocrystalline thin films date back to many decades. The most significant step towards the ellipsometric investigation of composite thin films was the realization of the first spectroscopic ellipsometers in the '70s [3, 4, 8], which allowed the measurement of the dielectric function, the imaginary part of which is directly related to the joint density of electronics states sensitively depending upon the changes of the crystal structure. The first models were based on the effective medium approach using constituents of known dielectric functions [5], whereas the volume fraction of the components can be related to the crystal properties of the thin films. This approach is popular ever since, based on its robustness.

The effective medium methods have been followed by a range of different analytical models based on the parameterization of the dielectric function. These models allow the determination of the material properties also in cases when the material cannot be considered as a homogeneous mixture of phases with known dielectric function. These models can also be used for small grains that show size effects (and hence a modified electronic structure and dielectric function), i.e. for grains that can not be modeled by bulk references.

Additional to the nanocrystal properties, the ellipsometric approach allows the sensitive characterization of further layer characteristics like the interface quality (e.g. nanoroughness at the layer boundaries), the lateral or vertical inhomogeneity or the thicknesses in multi-layer structures.

2. Basics of ellipsometry

If polarized light will be reflected on the boundary of two media, the state of polarization of the reflected beam will be elliptical, circular, or linear depending on the properties of the sample. In most cases, the reflected light is elliptically polarized, that's why the method is

called ellipsometry. Ellipsometry directly measures the change of polarization caused by the reflection, i.e. the complex reflectance ratio defined by

$$\rho = \frac{\chi_r}{\chi_i} = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta}, \quad (1)$$

where $\chi_r = E_{r,p}/E_{r,s}$ and $\chi_i = E_{i,p}/E_{i,s}$ (r : reflected, i : incident; p : parallel to the plane of incidence; s : perpendicular to the plane of incidence) are the states of polarization with $E = E_0 e^{i(\omega t + \delta)} e^{-i\omega \frac{N}{c} x}$ describing the electromagnetic plane wave (ω : angular frequency; t : time; δ : phase; N : complex refractive index; c : speed of light; x : position), r_p and r_s are the reflection coefficients (the ratio of reflected and incident E values) of light polarized parallel and perpendicular to the plane of incidence, respectively, while Ψ and Δ are the ellipsometric angles [15, 17]. The latter are the raw data of an ellipsometric measurement usually plotted as a function of wavelength, angle of incidence, or time.

The sample properties like the layer thickness or the refractive index are determined using optical models, in which one assumes a layer structure and the refractive index of each layer at each wavelength. Using such optical models, the Ψ and Δ values can be calculated (for each wavelength and angle of incidence) and compared with the measured Ψ and Δ spectra. Next, the parameters of the optical model (e.g. thickness, refractive index, or parameters of the dispersion) are fitted using optimization algorithms like the Levenberg-Marquardt method in order to minimize the difference between the measured and calculated Ψ and Δ values.

3. Measurable nanocrystal properties

Ellipsometry can measure nanocrystals in a thin film form. The optical model consists of a substrate with usually known optical properties (e.g. single-crystalline silicon or glass) and one or more thin films containing the nanocrystals. The information needed to calculate the ellipsometric angles Ψ and Δ (that in turn can be compared with the measured angles) are the angle of incidence, the thickness(es) of the layer(s) and the complex refractive indices of each medium. The square of the refractive index is the dielectric function, the imaginary part (ϵ_2) of which is directly proportional to the joint density of electronic states of the measured crystalline or partly crystalline material. Compared to the typical sensitivities ($< 10^{-3}$ in ϵ) the difference between the dielectric functions of the amorphous and single-crystalline phases are huge, as shown in Fig. 1. It is clearly seen that the dielectric functions are largely different depending on the crystallinity of silicon ranging from single-crystalline through nanocrystalline to amorphous. Note that the sensitivity is especially high around the critical point energies, which appear as peaks in ϵ_2 . For example, the difference of the three cases in ϵ_2 is larger than 10 at the critical point energy of 4.2 eV.

The key of measuring nanocrystals is to relate the dielectric function to nanocrystal properties. The technique that is most widely used for more than 30 years is the effective medium theory [5, 10]. In this theory it is assumed that the material is a mixture of phases large enough to retain their bulk-like properties, but smaller than the wavelength of the probing light, so that scattering can be avoided. In case of a mixture of two components with dielectric functions of ϵ_a and ϵ_b the effective dielectric function (ϵ) can be determined using effective medium theory, the most general form of which is the self-consistent Bruggeman effective medium

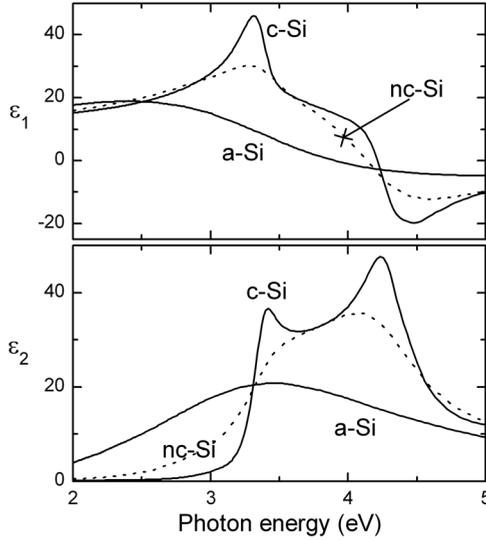


Figure 1. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of single-crystalline (c-Si), amorphous (a-Si), and nanocrystalline (nc-Si) silicon.

approximation (B-EMA):

$$0 = f_a \frac{\epsilon_a - \epsilon}{\epsilon_a + 2\epsilon} + f_b \frac{\epsilon_b - \epsilon}{\epsilon_b + 2\epsilon}. \quad (2)$$

The fit parameters of such models are the volume fractions f_a and f_b of components a and b , respectively (ϵ_a and ϵ_b are known, ϵ is calculated assuming f_a and f_b values). In turn, the change of the volume fractions can be related to the morphological changes of the material.

As an example of using B-EMA, let's consider an intensively investigated nanocrystalline material, namely the nanocrystalline silicon prepared by a range of deposition techniques from low temperature chemical vapor deposition to magnetron sputtering. A typical optical model for the measurement of this material uses components of single-crystalline silicon (c-Si, dielectric function from Ref. [16]), amorphous silicon (a-Si, dielectric function from Ref. [6]), nanocrystalline silicon (nc-Si, dielectric function from Ref. [18]), and voids. Some optical models for large-grain (Model 1) and small-grain (Model 2) nanocrystalline silicon layers deposited on oxidized single-crystalline silicon wafers are shown in Fig. 2 (see also Ref. [25]). The surface nanoroughness is also considered as a homogeneous layer [9], the thickness of which correlates with the root mean square roughness [22]. There are more sophisticated theories to analyze the surface roughness from the polarized optical response [14], but the robustness of the above effective medium approach makes it a popular, most widely used method. Note however, that the accurate, validated determination of the root mean square roughness is a problem even by scanning probe methods, because the obtained numerical

value may strongly depend on the measurement configuration (e.g. the window size or the quality of the tip, [22]).

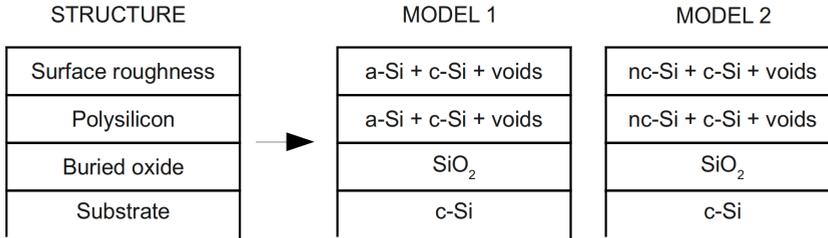


Figure 2. Some B-EMA models for nanocrystalline Si on c-Si with different expected grain sizes. Models 1 and 2 can be used for large and small grain sizes, respectively.

In Fig. 2 both the surface nanoroughness and the bulk layer properties are described by a combination of a-Si, c-Si, and voids or nc-Si, c-Si, and voids. The voids ratio serves as a density correction in the bulk layer, and it describes the character of the surface nanoroughness in the roughness layer. In many cases, the void ratio is fixed at 50 % due to a possible correlation with the thickness of the surface roughness layer. The model also contains the buried thermal oxide. The thickness of this oxide layer can also be determined in one fitting step together with the volume fractions of the components in the roughness and bulk nanocrystalline silicon layer, as well as their layer thicknesses.

For layers with smaller nanocrystals (several times 10 nanometers or below) the use of the nc-Si reference dielectric function [18] provides a better fit than using the conventional components of c-Si, a-Si, and voids. The volume fraction of the nc-Si component in the model is an indication of the crystallinity (Fig. 3). The higher the volume fraction of the nc-Si component, the smaller the grain size [25]. The sensitivity is revealed to be high, however, quantitative measurements verified by reference methods were not performed. Micrographs of transmission electron microscopy were available, but the technique of a reliable grain size analysis using image processing is missing.

There are a range of methods for the analytical representation of the dielectric function of semiconductors. A general empirical approach is to use a combination of Lorentz oscillators. This method allows the determination of the critical point energies and the layer thickness [13].

The critical point features can also be characterized by calculating the derivative of the dielectric function [7]. Using this approach the broadening of the critical point features can especially well be characterized. In turn, the grain size can indirectly be measured, because the broadening is proportional to the electron scattering at the grain boundaries, i.e. the amount of grain boundaries is measured.

The generalized oscillator model applies a standard analytical equation for all types of critical points [11]. The dimensionality of the critical point can be adjusted by a parameter of the model.

Another general approach for the parameterization of the critical point features of the dielectric function is the generalized critical point model suggested by B. Johs et al. [19]. In this model the dielectric function around the critical point is described by four Gaussian-broadened polynomials. A detailed description can be found in Ref. [12].

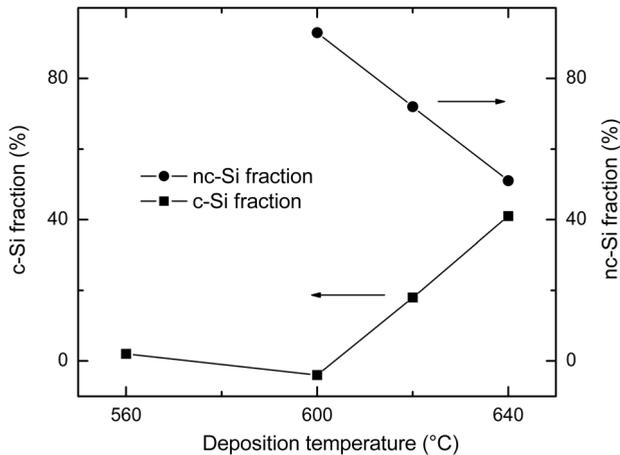


Figure 3. c-Si and nc-Si volume fractions as functions of the deposition temperature. The grain size increases with increasing temperature. Reprinted with permission from Journal of Applied Physics 87, P. Petrik, Ellipsometric study of polycrystalline silicon films prepared by low-pressure chemical vapor deposition, 1734 (2000). Copyright 2000, American Institute of Physics.

A special parameterization has been developed by S. Adachi. This model dielectric function describes each critical point with a specific analytical equation depending on the type of the critical point [1, 26]. As a result, one has a set of Kramers-Kronig-consistent analytical equations, with each equation describing an oscillator. The superposition of all the fitted oscillators results in the final dielectric function as shown in Fig. 4. It is also shown that the effective medium approximation using the combination of c-Si and a-Si as described above doesn't allow an acceptable fit (short-dashed line). Although the number of parameters to fit is large, there are a lot of possibilities to couple or fix non-sensitive parameters [23].

The most important properties of the nanocrystal layers that can be measured by ellipsometry are the layer thickness and the grain size (Table 1). The crystallinity can be defined for ellipsometry as the "position" of the dielectric function between that of the single-crystalline and the amorphous ones. In terms of effective medium theory this can be defined as the c-Si to a-Si ratio of the model components. The density is also a parameter that can be expressed compared to a reference value. Staying at the above example the model "c-Si + a-Si + void" compares the density to the purely "c-Si + a-Si" case.

Additional to the above parameters a range of thin film-related parameters can be determined. Most important may be the vertical inhomogeneity and the interface quality. Using ellipsometry it can sensitively be checked whether the layer is of optical quality.

4. Applications

The range of ellipsometric applications for nanocrystals is very large. The most important applications comprise semiconductor nanocrystals, with silicon still being the number one.

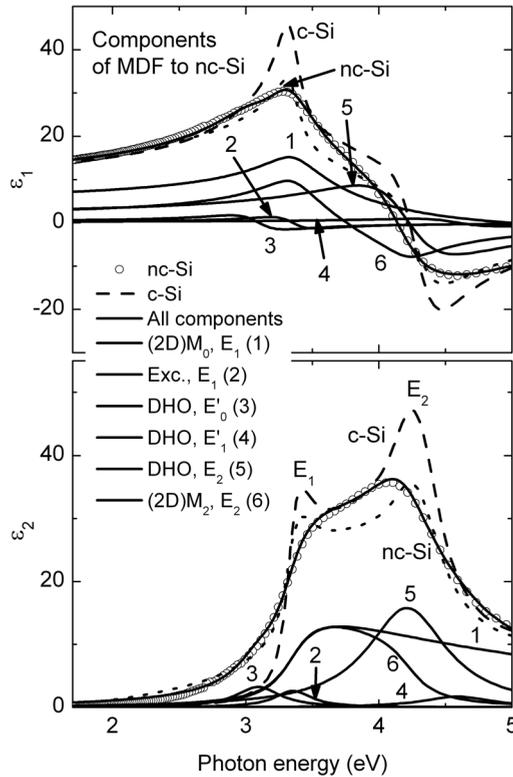


Figure 4. Oscillators of the model dielectric function of S. Adachi (numbered solid lines) fitted to the reference dielectric function of a fine-grained polycrystalline silicon (nc-Si). The long-dashed line is the single-crystalline silicon (c-Si) reference. The short-dashed line shows the fit using the effective medium approximation described above with the components of c-Si and a-Si.

In this section some relevant applications known to the author are selected, with no claim to completeness.

The correlation between the grain size and the broadening of the dielectric function at the E_1 critical point was revealed by H. V. Nguyen and R. W. Collins in an in situ study during plasma enhanced chemical vapor deposition [21]. The grain size was determined from the layer thickness assuming a three-dimensional, isolated particle growth. It was shown that the theoretically predicted relationship that the broadening is proportional to $1/d$, where d denotes the grain size, holds for the investigated nanocrystals (Fig. 5). Furthermore, the extrapolation of $d \rightarrow \infty$ results in the expected broadening value of the single-crystalline silicon, which suggests that this behavior is valid for smaller crystals as well. It is important to note that the investigated thickness range of 20–25 nm was large enough to neglect the shift of the critical point energy due to the quantum confinement.

G. F. Feng and R. Zallen [13] used Raman spectroscopy to verify the linearity between broadening and reciprocal grain size (Fig. 6) on nanocrystals created by ion implantation in

Property	Notes
Grain size	Sub-nanometer sensitivity Indirect: "calibration" needed
Crystallinity	Amount of grain boundaries In case of one-phase layers indicative to grain size
Layer thickness	Sub-nanometer sensitivity Also in multi-layers
Density	Compared to the reference materials used in the model
Inhomogeneity	Both vertical and lateral
Interface quality	Whether one needs an additional transition layer to achieve a good fit
Surface nanoroughness	As a homogeneous roughness layer or using more sophisticated methods
Shape of crystals	In principle possible using anisotropy and B-EMA screening

Table 1. Properties of nanocrystal layers that can be measured by ellipsometry.

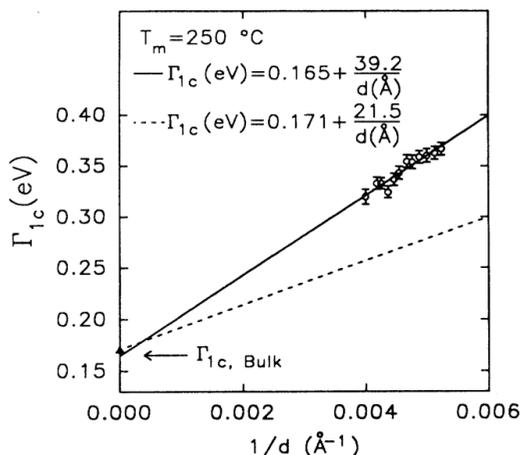


Figure 5. Broadening of the dielectric function at the E_1 critical point energy for grain sizes of d measured during layer growth. Reprinted from Physical Review B 47, H. V. Nguyen and R. V. Collins, Finite-size effects on the optical functions of silicon microcrystallites: A real-time spectroscopic ellipsometry study, 1911 (1993). Copyright 1993, American Physical Society.

GaAs in the size range of 5-50 nm. A good linearity was found for all investigated critical point energies. This example also proves that the sensitivity is high enough, and the quantitative determination of the grain size is possible by validation using a reference method.

A further example of a nanocrystalline structure is porous silicon prepared by electrochemical etching. After etching, the sample has a well-defined nanostructure depending on the etching conditions. The size of the remaining nanocrystals strongly depends on the doping level of the substrate. In the study of P. Petrik et al. [23] substrates with different B-doping were used

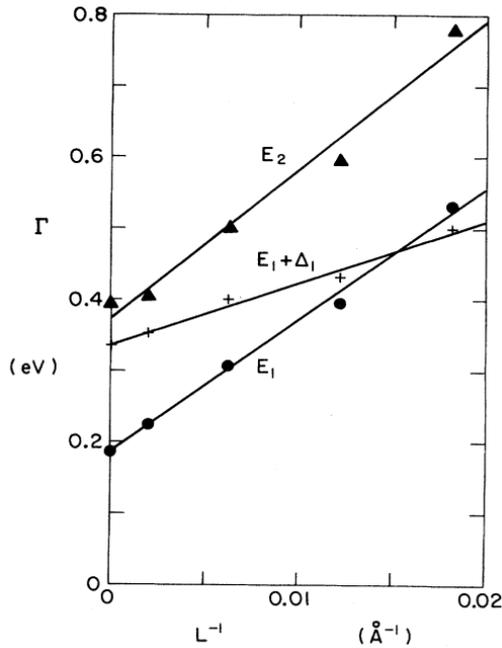


Figure 6. Broadening of the dielectric function at different critical points as a function of the reciprocal crystallite size in ion implanted GaAs. Reprinted from Physical Review B 40, G. F. Feng and R. Zallen, Optical properties of ion-implanted GaAs: The observation of finite-size effects in GaAs microcrystals, 1064 (1989). Copyright 1989, American Physical Society.

to achieve substrate resistivities from 0.01 to 0.09 Ωcm and nanocrystal sizes from 3 to 12 nm. In case of porous silicon the use of proper optical models is of crucial importance, because the layers are usually vertically non-uniform. In this study the dielectric function of the porous silicon layers were analyzed using the model dielectric function of S. Adachi described above. The fitted broadening parameters of the model are plotted as a function of the grain size in Fig. 7. Similar to the above cases, a more or less systematic behavior was found also in this study, especially for the E_1 critical point (Γ_1). The reason is that the porous silicon layers are vertically inhomogeneous, and the information depth (in c-Si) at the E_1 and E_2 critical point energies are about 30 and 10 nm, respectively. So Γ_2 is very sensitive to surface deteriorations. The dependence on the layer thickness is also due to the vertical gradient in the nanostructure.

Chemical vapor deposition combined with oxidation was used to prepare nanocrystal layers with well-defined grain sizes [20]. The thin nanocrystal films were deposited on quartz substrates, and the nanocrystal size was set by the layer thickness and the time of the oxidation process, with nanocrystal sizes verified by electron microscopy and X-ray diffraction. For the analysis of the nanocrystal layers the above mentioned effective medium approximation could successfully be applied using a combination of nc-Si, c-Si, and SiO_2 reference dielectric functions [2]. It was shown that the nanocrystallinity defined by $f_{nc-si}/(f_{c-si} + f_{nc-si})$, where f denotes the fitted volume fractions of the components (see equation 2), correlates well with the nanocrystal size determined by the layer thickness (see Fig. 8). This example

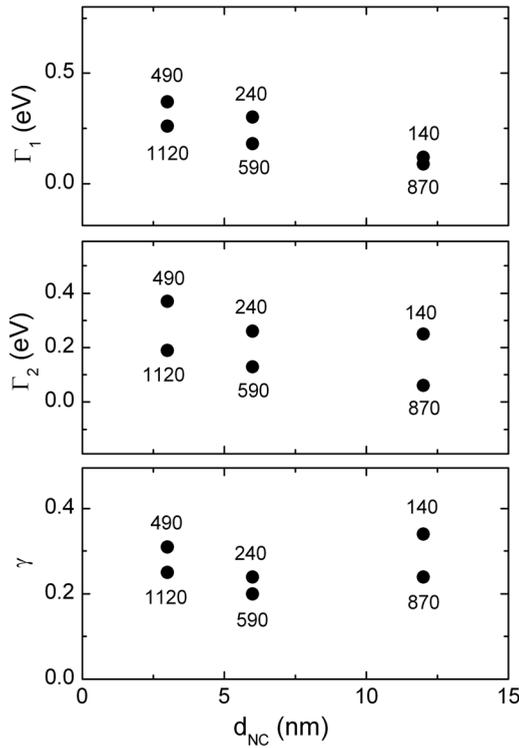


Figure 7. Broadening values measured using the model dielectric function of S. Adachi for different grain sizes (d_{NC}). The numbers at the measured points show the thicknesses of the measured layers. Reprinted from Journal of Applied Physics 105, P. Petrik et al., Nanocrystal characterization by ellipsometry in porous silicon using model dielectric function, 024908 (2009). Copyright 2009, American Institute of Physics.

also shows that the nanocrystal size can sensitively (though indirectly) be measured by this optical technique.

The importance of an optical technique is not only the speed and sensitivity, but also the in situ capability. Using special beam-guiding techniques the ellipsometric measurement can even be made in a vertical furnace through the base plate (i.e. without modifying the furnace walls) [24]. The performance of current computers allows a real time evaluation of the process, providing the layer thicknesses and the information on the morphology. Fig. 9 shows the results of an in situ measurement made in a vertical furnace during crystallization of a deposited amorphous layer. The thickness of the amorphous silicon layer was about 40 nm, deposited on a thermally oxidized (10 nm oxide) silicon wafer. Accordingly, the optical model consists of a single-crystalline silicon substrate, a buried SiO₂ layer (with a thermal SiO₂ reference dielectric function), an initially amorphous silicon layer described by the a-Si reference, and an SiO₂ surface oxide layer. The surface roughness could be neglected for the deposited amorphous silicon layer. During annealing crystals are formed in the amorphous silicon layer. This can be followed by a simple effective medium combination of components

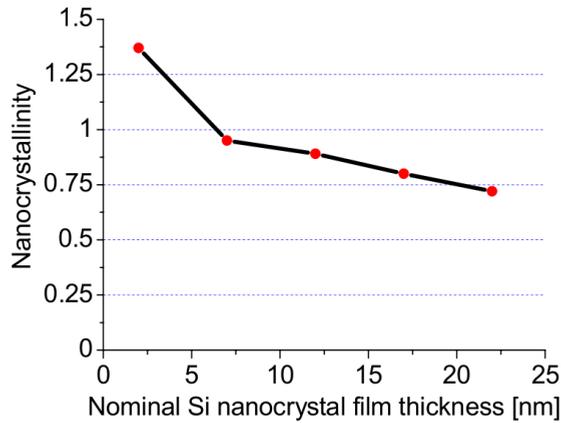


Figure 8. Nanocrystallinity as a function of the thickness of nanocrystal films prepared by chemical vapor deposition and oxidation of quartz substrates. Reprinted from Mater. Res. Soc. Symp. Proc. 1321, E. Agocs et al., Optical characterization using ellipsometry of si nanocrystal thin layers embedded in silicon oxide, DOI: 10.1557/opl.2011.949. Copyright 2011, Cambridge University Press.

a-Si and c-Si, as described above. The increasing volume fraction of c-Si represents the process of crystallization during annealing (see Fig. 9).

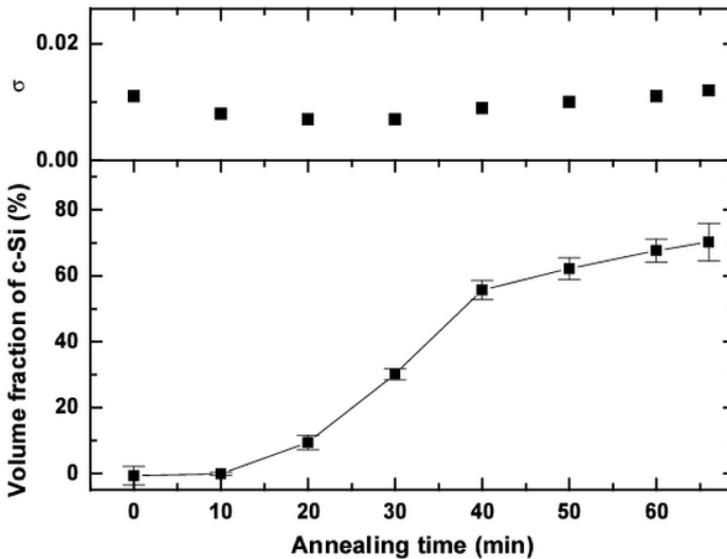


Figure 9. Fitted volume fraction of crystalline silicon in the effective medium model as a function of annealing time. Reprinted from Thin Solid Films 364, P. Petrik et al, In situ spectroscopic ellipsometry for the characterization of polysilicon formation inside a vertical furnace, 150 (2000). Copyright 2000, with permission from Elsevier.

5. Conclusions

The capability of measuring the change of phase by the reflection of polarized light on a surface or layer structure allows a typical sensitivity of less than one nanometer for the layer thickness and $10^{-3} - 10^{-4}$ for the refractive index. These capabilities together with a spectroscopic use in the photon energy range of the characteristic interband transitions makes the method applicable for an accurate determination of nanocrystal properties especially for Si, but also for wide band gap semiconductors using an extension into the deep UV spectral range. The sensitivity is high down to the smallest nanocrystal sizes. The requirement for an accurate nanocrystal measurement is a layered form with optical quality interfaces. The thickness, homogeneity and interface qualities of the layers can be measured directly, whereas the properties related to the nanocrystal structure (like the crystallinity, the nanocrystal size or the density of the layer) can be obtained indirectly using proper optical models and "calibration" by reference methods.

Author details

Peter Petrik

Institute for Technical Physics and Materials Science (MFA), Research Centre for Natural Sciences, Konkoly Thege u. 29-33, 1121 Budapest, Hungary

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