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Optical study of microvoids, voids, and local inhomogeneities in amorphous silicon

M. Vanecek
Institute of Physics, Czechoslovak Academy of Sciences, Cukrovarnicka 10, Prague 6, Czechoslovakia

J. Holoubek
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 16206 Prague 6, Czechoslovakia

A. Shah
Institute of Microtechnology, Neuchâtel University, Breguet 2, CH-2000 Neuchâtel, Switzerland

Elastic light scattering has been used for a study of microstructure in amorphous hydrogenated silicon. A simple theory to get quantitative informations on the microstructure has been presented for the first time, both for Rayleigh and Mie scattering. For optimal very high frequency glow discharge amorphous silicon layers, the presence of voids with diameter between 1 and 20 nm is typical.

It is now well established that considerable microstructure exists in hydrogenated amorphous silicon (a-Si:H): this follows from an extensive investigation of microstructure by transmission and scanning electron microscopy,[1] small angle scattering experiments,[2] from studies of hydrogen distribution by calorimetry,[3] and by nuclear magnetic resonance.[4] Recently, it has been confirmed that even high-quality glow discharge amorphous silicon, which yields solar cell efficiencies well above 10%, has its microstructure. Studies by small angle x-ray scattering (SAXS) together with density measurements give direct evidence that 10^{19} cm^{-3} microvoids with diameters of about 1 nm are present in these films.[5] There exist now many attempts to relate the local microstructure with the light-induced degradation of a-Si:H (Staebler–Wronski effect).[6] Thus, each quantitative method elucidating the microstructure of a-Si:H is potentially of great importance, especially if it is simple in its application and if it is also compatible with solar cell technology (deposition of about 1 μm of a-Si:H on a glass substrate). In a recent paper[7] we have suggested a simple new method for measuring the light scattering coefficient (turbidity) in thin a-Si:H films. We have now started to measure the spectral dependence of the light scattering coefficient α_s in amorphous silicon in $\lambda = 0.9$–$1.4\ \mu$m region.[8] Here, we present a quantitative theoretical description of elastic light scattering (ELS) (Rayleigh and Mie scattering), appropriate to amorphous silicon thin films. On the basis of this theory we quantitatively discuss our experimental data on α_s (Refs. 7 and 8) and give typical void sizes and concentrations for high-quality [very high frequency glow discharge (VHF-GD)][9] amorphous silicon.

Scattering losses may be caused by any of several contributing factors. In films with negligible surface and interface scattering the observed volume scattering is due to heterogeneities in refractive index. Local fluctuations in the refractive index can be induced by stress, microvoids, voids, microcrystallites, or by any lower or higher density region in a-Si:H films. Total extinction (attenuation) of radiation is described[10] by the extinction coefficient α_e

$$\alpha_e = \alpha_a + \alpha_s \qquad (1)$$

where α_a is the optical absorption coefficient and α_s is the scattering coefficient. It is well established that the scattering losses can be expressed in terms of the scattering coefficient (turbidity) as[11]

$$\alpha_s = \alpha_R + \alpha_M + \alpha_i \qquad (2)$$

where $\alpha_R = A/\lambda^4$ is the scattering loss connected with Rayleigh scattering, α_M is the Mie scattering contribution that possesses a wavelength dependence between λ^2 and λ^{-2} and α_i is wavelength-independent scattering. We will look for a possible range of α_s and its spectral dependence, for defects of various sizes both in the Rayleigh and Mie scattering regions, and with different densities. To start with a simple model, we will first identify the dominating scattering centers with voids in device quality material.[5,12] Later we will discuss also other types of inhomogeneities. So, we assume that scattering centers are spheres (voids with refractive index close to 1) randomly distributed in the medium; the latter has a refractive index equal to that of bulk amorphous silicon in a very weak absorption region (approximately equal to 3.5). We start with the explicit relation between the scattering coefficient and other optical parameters in the form[10]

$$\alpha_s = N_s(\pi a^2)Q_{\text{sca}} = N_s C_{\text{sca}}, \qquad (3)$$

where N_s is the number of scatterers per cm^3, a is the radius of the sphere, and Q_{sca} the scattering efficiency factor. Finally, C_{sca} is the scattering cross section. Q_{sca} can be easily calculated for spheres that are small with respect to the wavelength both outside and inside the scatterer (in the Rayleigh region). The scattering behavior is similar for all scatterers with sizes smaller than about $\lambda/10$ (that is $\lambda_{\text{vac}}/35$ in a-Si:H; so about 30 nm for $\lambda_{\text{vac}} = 1\ \mu$m). For nonabsorbing spheres in the Rayleigh region, we have[10]

$$Q_{\text{sca}} = 8/3x^4(m^2-1)^2/(m^2+2)^2, \qquad (4)$$

where $x = (2\pi a m_2)/\lambda_{\text{vac}}$ is the size parameter, m_2 is the real part of the refractive index of the outside medium,

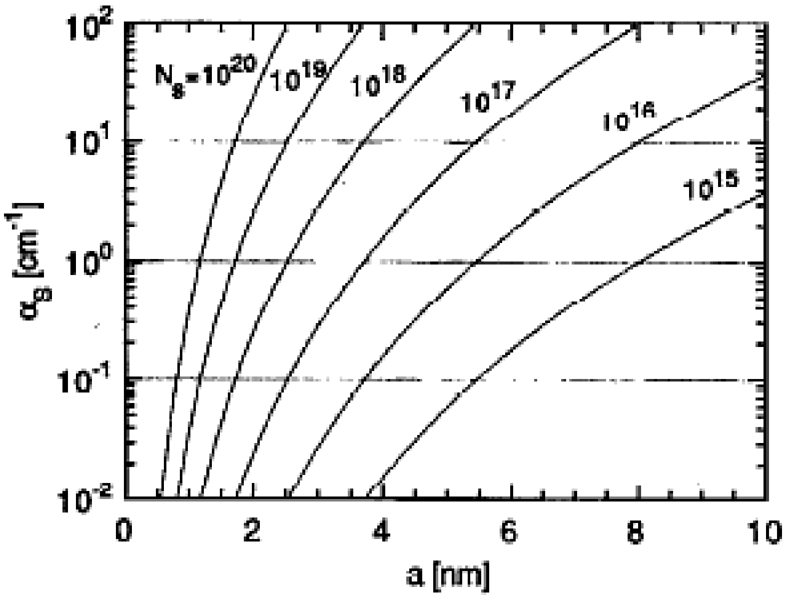

FIG. 1. Dependence of the optical scattering coefficient α_s (at the wavelength $\lambda = 1$ μm) on the void radius a. Concentration of the voids N_s is the parameter.

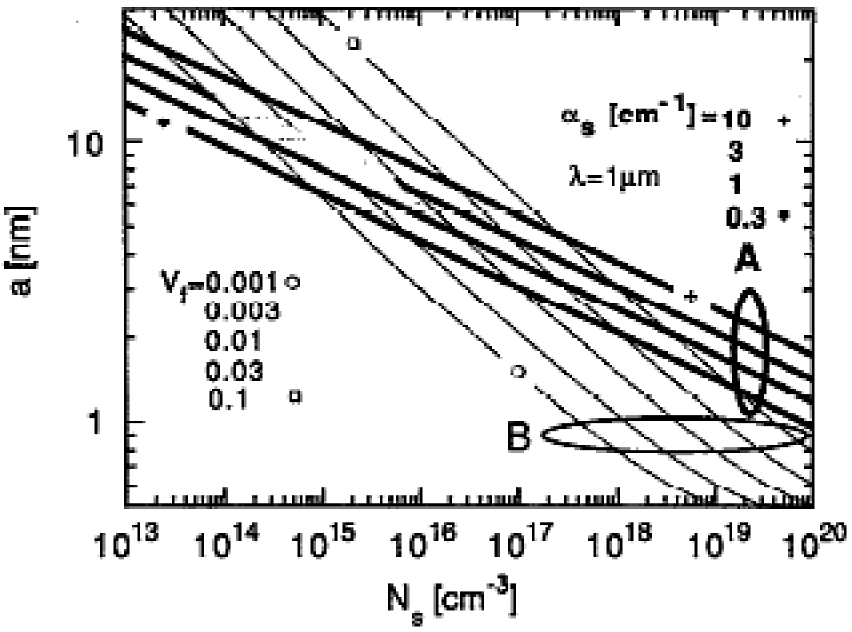

FIG. 2. Determination of the void radius a and their concentration N_s from the value of the optical scattering coefficient α_s at $\lambda = 1$ μm and from the void fraction v_f. The set of curves A represents solution of Eqs. (3) and (4), the set of curves B represents solution of Eq. (6). The shaded area marks the range of typical good quality VHF-GD samples.

λ_{vac} is the wavelength of light in vacuum, m the relative refractive index ($m = 1/m_2$ in the case of a void).

For scatterers larger than about $\lambda/10$, the simple relation (4) must be replaced by the exact Lorenz–Mie expression which holds for spherical scatterers of arbitrary size and refractive index.[10] The explicit relation for Q_{sca}

$$Q_{\text{sca}} = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n+1)(|a_n|^2 + |b_n|^2), \tag{5}$$

is now in the form of an infinite series of partial waves contributing to total scattered intensity. The calculated values of Q_{sca} given in this letter are based on the published program BHMIE.[13]

To discuss the simplest but realistic[5,12] case of small voids, which can be considered to be Rayleigh scatterers, we calculated α_s according to Eqs. (3) and (4). The results are summarized in Fig. 1. It can be seen that the experimentally observed range of optical losses can be obtained by various combinations of appropriate sizes and concentrations of spherical voids. To choose the correct combination of void size and concentration, an independent determination of the void fraction v_f is necessary (this can be obtained from the film density measurement[14] or from SAXS data[5]). This is demonstrated in Fig. 2. The set of curves (A) gives us solutions of Eqs. (3) and (4), α_s being the parameter. Another set of curves (B) gives solutions of Eq. (6), the void volume fraction v_f being now the parameter:

$$N_s n_v = v_f N_{\text{Si}}, \tag{6}$$

where n_v is the number of silicon atoms missing in the void (proportional to a^3) and N_{Si} is the number of silicon atoms per cm^3 ($\sim 5 \times 10^{22}$ cm^{-3}). Precision in the determination of the voids size and concentration from ELS data is given by the accuracy of the void fraction measurement.[5,14] As can be seen from Fig. 2, the void size can be deduced much more accurately than the void concentration. As concerns the effect of interactions between dense agglomerates of voids, the calculation[13] indicates that the interactions are negligible for a separation of scatterers greater than three diameters (a condition that is in average fulfilled for a void fraction $v_f < 0.015$). This is typical for good quality a-Si:H.[16]

When the void size starts to increase, we will get, already at the radius $a = 20$ nm, a distinct departure from the $1/\lambda^4$ dependence of α_s. This is demonstrated in Table I, where scattering cross sections and their spectral dependence were calculated by means of the BHMIE program.[13] In Table I it is shown how the same value of $\alpha_s(\lambda = 1$ μm) can be obtained for different combinations of the void radius a and concentration N_v, and how the void fraction v_f (in the Rayleigh region) and the exponent k in the spectral dependence term $\alpha_s(1/\lambda^k)$ (in Mie region) give us necessary supporting data to choose a proper combination of N_v and a.

In our calculations we should not limit ourselves just to one type of the scatterer—the void. We will therefore

TABLE I. Combinations of void parameters (a is the void radius and N_v is the number of voids per cm^3) yielding the same scattering coefficient α_s at $\lambda = 1$ μm. Scattering cross section C_{sca}, power k of the wavelength dependence $\alpha_s(1/\lambda^k)$, and the corresponding void fraction v_f are also given.

a (nm)	N_v (cm^{-3})	C_{sca} (cm^{-2})	α_s (cm^{-1})	k	v_f
1	7.9×10^{20}	3.8×10^{-21}	3.00	4.0	···
1.5	6.9×10^{19}	4.3×10^{-20}	3.00	4.0	≈0.7
3	1.1×10^{18}	2.7×10^{-18}	3.00	4.0	0.106
5	5.0×10^{16}	5.9×10^{-17}	3.00	4.0	0.024
10	8.3×10^{14}	3.6×10^{-15}	3.00	3.9	3.3×10^{-3}
15	8.2×10^{13}	3.7×10^{-14}	3.00	3.8	1.1×10^{-3}
30	1.6×10^{12}	1.8×10^{-12}	3.00	3.3	1.8×10^{-4}
50	1.3×10^{11}	2.3×10^{-11}	3.00	2.6	6.8×10^{-5}
100	7.8×10^{9}	3.8×10^{-10}	3.00	1.6	3.3×10^{-5}

discuss now other possible inhomogeneities which could be expected in amorphous silicon, especially for layers grown under nonoptimal conditions.[1,2,4] These are islands of material with a different refractive index from that of the rest of the bulk. The scattering cross section C_{sca} depends on the magnitude of the relative refractive index [see Eq. (4)]. For example, if the refractive index of the islands is equal to 2 (typical value for polysilane regions), C_{sca} decreases just 2.3 times. Thus, the voids can contain some polysilane $(SiH_2)_n$ chains without a large change in their light scattering properties. If the refractive index fluctuates just slightly, for example, from 3.5 to 3 in the island (or fluctuates even more weakly for microcrystalline silicon inclusions), C_{sca} decreases 20 times (or much more in the latter case) compared to the case of void.

To give specific information on amorphous silicon, we will briefly discuss our experimental data on VHF-GD amorphous silicon:[7,8]

(1) Measured values of $\alpha_s(\lambda = 1\ \mu\mathrm{m})$ range from 0.5 to 10 cm^{-1}. Thus, as can be deduced from data in Table I, the observed density deficiency has to be due only to small voids ($a < 15$ nm).

(2) If there is in reality a distribution of void sizes, the measured value of $\alpha_s(\lambda)$ is a weighted integral of the void size distribution multiplied with the respective scattering cross-sections. It follows from Eqs. (3) and (4) that α_s will then be dominated by the larger voids. Fortunately, at $a > 20$ nm the spectral dependence of α_s starts to deviate from the $1/\lambda^4$ law (Table I) as we have experimentally observed[8] in the case of nonoptimal samples. Thus we can obtain additional information on void or inhomogeneity size distribution.

(3) Our optimal (low deep defect density) samples[8] deposited at 200 °C have approximately a $1/\lambda^4$ spectral dependence.[8] With $v_f = 0.001$–0.01 and $\alpha_s(\lambda = 1\ \mu\mathrm{m}) = 3$ cm^{-1}, this gives us approximately a void radius $a = 10$ nm for these large voids, and the value for the concentration of these voids as $N_s = 10^{15}\ \mathrm{cm}^{-3}$. This is in good agreement with preliminary SAXS measurements, which point to a void distribution with sizes ranging from $a = 0.5$ to 10 nm in VHF-GD samples grown under the same conditions.[16] This situation is different from that observed in some conventional GD (13.56 MHz) device quality samples where microvoids with diameter 1 nm are fully dominant,[5] and ELS is below the detection limit[8] but it corresponds to recent observations of larger voids in the case of remote hydrogen plasma chemical vapor deposition device quality amorphous silicon.[12]

To conclude, we have presented a simple theory that enables us to obtain quantitative information on microstructure in amorphous silicon from the optical elastic light scattering (ELS) coefficient and its spectral dependence. ELS has the advantage of being a simpler experimental method than SAXS; however, it has the disadvantage of giving only an upper limit for the void size in the material. For optimal VHF-GD amorphous silicon the presence of voids with diameters between 1 and 20 nm is typical.

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