

Optical absorption coefficient of polycrystalline silicon with very high oxygen content

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Abstract

We report measurements of the room temperature optical absorption coefficient $\alpha(\lambda)$ of polycrystalline silicon ribbon material with high oxygen concentration (1.7×10^{18} at. cm^{-3}) in the spectral range from 800 to 1200 nm. Between 800 and 1000 nm, absolute error is estimated as $\approx 2\%$. Sample to sample variations in this range are $\pm 2\%$, and differences from Czochralski control samples are also within 2%. Within the experimental error, the $\alpha(\lambda)$ for our ribbon samples is indistinguishable from that of monocrystalline silicon between 800 and 1000 nm. Our data are well fitted in this region by $\alpha(\lambda) = (85.6/\lambda - 77.7)^2$, with λ in μm and α in cm^{-1} . Although the experimental error rises sharply at longer wavelengths due to maximum ribbon thickness of only 450 μm , we can state that our results are consistent with the data compiled by Green [1] between 800 and 1200 nm for pure monocrystalline silicon.

Keywords: Silicon; Optical properties; Solar cells

1. Introduction

The original motivation for this work was the need to check the quality of polycrystalline silicon ribbons produced in our laboratory. Ribbons are grown from a molten zone within an oxide cap, and retain dissolved oxygen with a concentration equal to the solubility limit at the melting temperature, i.e. 1.7×10^{18} at. cm^{-3} , as measured by infrared spectroscopy [2].

The minority carrier diffusion length, L , the most significant single parameter for assessment of material quality as a substrate for photovoltaic solar cells, is usually obtained from the spectral response of surface photovoltage or cell short-circuit current measurements. In order to extract L from these measurements, one needs precise knowledge of the optical absorption coefficient $\alpha(\lambda)$ in an appropriate spectral domain, for silicon, the range between 800 and 1000 nm. The optical absorption coefficient of silicon in that range has been measured by several authors [3–7]. The differences among the published data, however, lead to significantly different L values for the same set of spectral response

measurements. For monocrystalline pure silicon there are generally accepted sets of data on $\alpha(\lambda)$, such as those compiled by Green [1]. However, our silicon material is multicrystalline, has a very high oxygen content, and it certainly retains residual stresses (although care has been taken in furnace design to minimize them). The unknown effect of these deviations from perfection on the absorption coefficient would lead to large uncertainties in L , and justifies independent measurements of $\alpha(\lambda)$ in our material. Although not strictly necessary for the extraction of L from spectral response data, we decided to extend our measurements to the interesting sub-gap region up to 1200 nm.

2. Experimental procedure

2.1. Sample preparation

In the wavelength range of interest, the absorption coefficient varies by several orders of magnitude; to reach a high precision, samples of different thicknesses must be used. Therefore eight samples of thicknesses between 50 and 450 μm (the maximum for as-grown

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ribbons) were prepared by lapping and polishing, followed by chemical etching, essential to remove a surface film that seriously affects sample reflectivity. Care was taken to ensure that the chemical etching preserved parallelism and increased surface roughness only by a limited amount. Surface quality was always good enough for precise thickness determination by infrared interferometry.

2.2. Optical measurements

The absorption coefficient is experimentally obtained from

$$T^* = \frac{(1 - R)^2 e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} \quad (1)$$

where T^* is the effective transmission, which is directly measured, R the single surface reflectivity, and d the sample thickness. Reflectivity was also measured in the range from 800 to 1200 nm in order to avoid unnecessary assumptions. For a flat plate and for near-normal incidence

$$R^* = \frac{(1 - R)^2 R e^{-\alpha d}}{1 - R^2 e^{-2\alpha d}} + R \quad (2)$$

where R^* is the effective measured reflectivity. α and R are therefore obtained by simultaneous solution of Eqs. (1) and (2).

For most measurements of R^* and T^* we used an integrating sphere technique with monochromated (10 nm resolution) chopped light. This has the advantage of taking into account the possible spread of the transmitted or reflected beams. Small deviations from near normal incidence, after multiple passes inside the sphere, have negligible effect on R^* or T^* measurements. However, care must be taken to ensure that the sphere quality factor is not changed at all during the sample-in and sample-out measurement steps.

The reflected, or transmitted, optical signal was measured with a photodiode, coupled to a lock-in amplifier, with an integration time of 1 s, and signal fluctuations better than 1 part in 2000. Comparison of this technique with a conventional specular reflection procedure led to reproducible reflectivities always within 1%.

Absolute error for $\alpha(\lambda)$ has been estimated as 2% in the range 800–1000 nm. This is consistent with differences of $\pm 2\%$ in α obtained from different samples. However, errors rise sharply beyond 1000 nm, becoming $\approx 50\%$ at 1200 nm, due to the very low absorption coefficient, and to the limitation of maximum sample thickness of 450 μm .

3. Results

In Fig. 1, we show that our results for the reflectivity

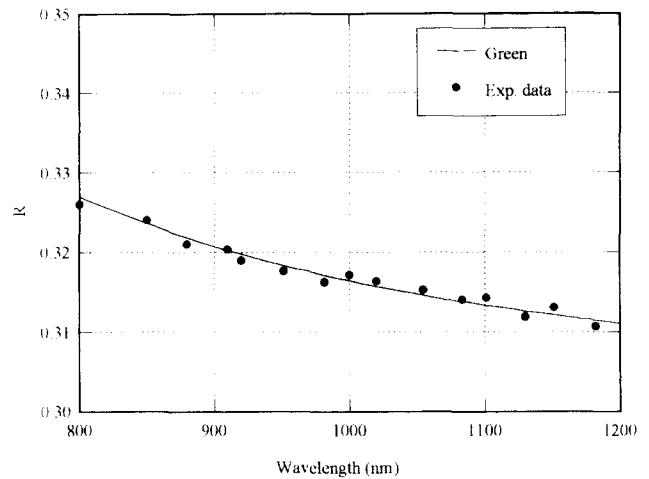


Fig. 1. Experimental reflectivity of oxygen-containing silicon ribbons (dots) and expected values (continuous line) calculated from the refractive index of pure silicon [1].

agree with those calculated from the index of refraction given in Ref. [1]. Standard deviation between the two sets of data is well below 0.5%.

From the display of our experimental $\alpha(\lambda)$ data and of those compiled by Green [1] in all the spectral range in Fig. 2, we notice a very good overall agreement except for the longest wavelengths, while the data of Dash and Newman [8], attributed to silicon with internal stresses, show a very distinct behaviour.

In the spectral range from 800 to 1000 nm, the most interesting for L determination, our data can be described by the relation

$$\alpha = \left[\frac{85.6}{\lambda} - 77.7 \right]^2 \quad (3)$$

where α is in cm^{-1} and λ the wavelength in μm , with a maximum deviation of 2% in this range. Our data agree

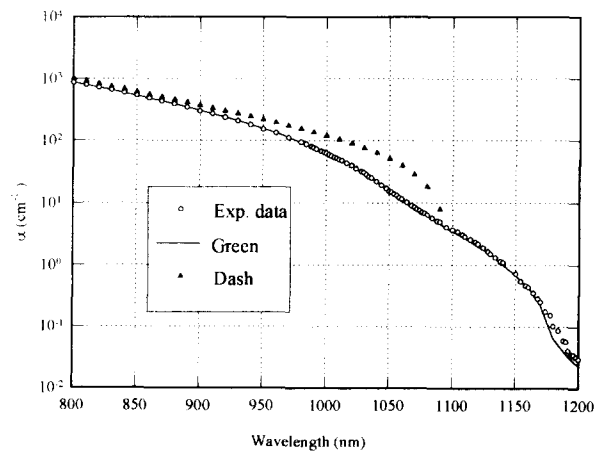


Fig. 2. Experimental optical absorption coefficient of our samples (open circles) compared to a compilation of data for pure silicon [1] (continuous line) and to the results of Dash and Newman [7] (triangles).

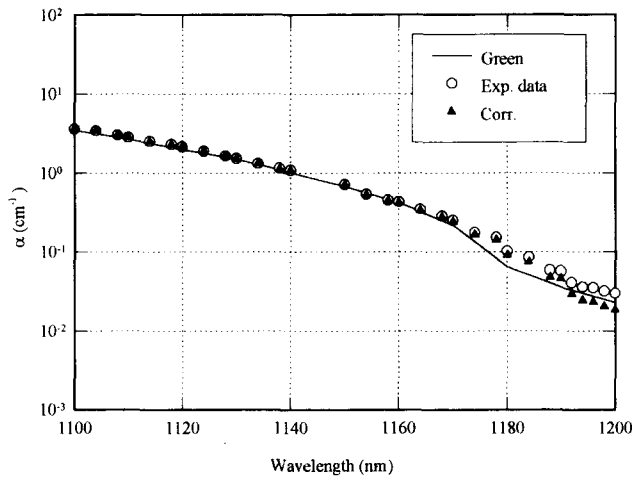


Fig. 3. Absorption coefficient in the range $1100 < \lambda < 1200$ nm. Uncorrected experimental results (open circles), corrected for free carrier absorption (triangles), and compiled data for pure silicon (continuous line).

best with those of Swimm and Dumas [4] (also used by Green in his compilation), who fitted their data with a similar function,

$$\alpha = \left[\frac{85.9}{\lambda} - 77.9 \right]^2 \quad (4)$$

Average deviation between the two functions is $\approx 1.7\%$, our α values being systematically smaller than theirs.

In order to check directly whether our material could be distinguished from monocrystalline silicon, a few samples of Czochralski single crystalline material were also measured in the same spectral domain; again no significant difference was found in $\alpha(\lambda)$ from our ribbon material.

In the spectral domain between 1000 and 1200 nm, free carrier (intraband) absorption may contribute to total α to a significant amount. For our p-doped silicon ribbons, with boron concentrations of $\approx 3 \times 10^{16}$ at. cm^{-3} , this contribution has been calculated and subtracted from the data, since we are particularly interested in absorption processes leading to electron–hole pair production. Fig. 3 demonstrates that this actually improves the agreement, generally well within experimental error, with the data compiled by Green.

Fig. 4 demonstrates that $\alpha(\lambda)$ can be fitted from 1.08 to 1.55 eV (1150 to 800 nm wavelength) by the simple law

$$\alpha = \frac{A}{1 - e^{-E_{\text{ph}}/kT}} [h\nu - E_g - E_{\text{ph}}]^2 + \frac{A}{e^{E_{\text{ph}}/kT} - 1} [h\nu - E_g + E_{\text{ph}}]^2 \quad (5)$$

with adjustable parameters A , E_g and E_{ph} . Such an expression could be expected for an indirect interband

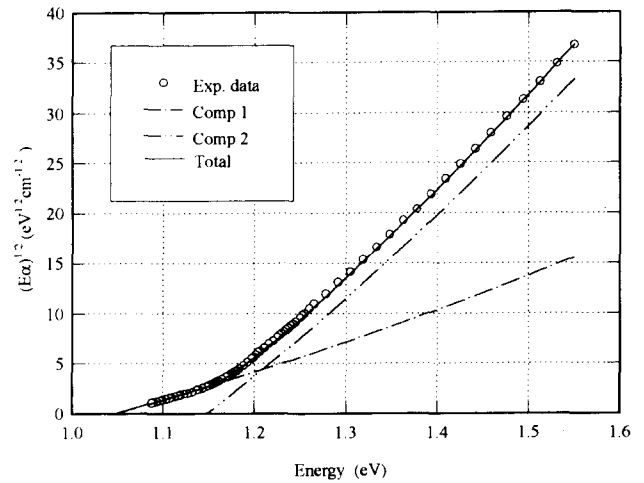


Fig. 4. Absorption coefficient: experimental results (open circles) and best fit performed using Eq. (5).

absorption edge, with the assistance of a single phonon of energy E_{ph} ; E_g would have the meaning of a bandgap. Actually at least 2 phonons are important, although the transverse optical mode (TO) is dominant [1,6], and multiple phonon processes play an increasing role at longer wavelengths. The fact that we can adjust this simple law for such a large photon energy range is quite remarkable. Nevertheless this is a semi-empirical fit, as demonstrated by the facts (i) that the ‘effective phonon’ energy, 50.8 meV, only approximates the value of 57.8 meV measured by neutron scattering and previously deduced by MacFarlane et al. [6]; (ii) the value obtained for the energy bandgap, 1.097 eV, is lower than the accepted value of 1.12 eV [1]; and (iii) deviations of the fitted curve for $\alpha(\lambda)$ from the experimental values are up to $\approx 10\%$ in the knee region.

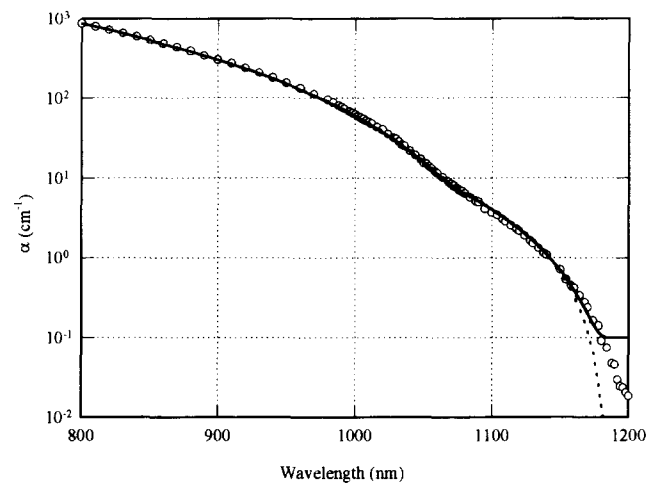


Fig. 5. Experimental absorption coefficient (open circles). The dotted line is the result of a fit with Eq. (5) (the best fit parameters are indicated in the text). The continuous line is a fit over 4 decades obtained using Eq. (5) with an added constant ($= 10^{-1} \text{ cm}^{-1}$).

Fig. 5 shows the result of the fit of Eq. (5) over all the range from 800 to 1200 nm, demonstrating that a reasonable description of α is possible over 3 orders of magnitude. The values of the fitted parameters are $A = 3825 \text{ cm}^{-1} \text{ eV}^{-2}$, $E_g = 1.0968 \text{ eV}$ and $E_{ph} = 50.8 \text{ meV}$.

Actually, description of the variation of α by 4 orders of magnitude is easily achieved by adding a constant to Eq. (5) (this has, of course, no physical meaning; it simply tells that α does not drop immediately to 0 for energies $h\nu < E_g - E_{ph}$). With an added constant of 10^{-1} cm^{-1} , and using the fitted parameters indicated above, we can describe our data for α , within $\approx 10\%$, between 10^3 and 10^{-1} cm^{-1} , i.e. λ between 800 and 1175 nm.

4. Conclusions

Unlike other authors [4,7] who found differences between the optical absorption coefficient of pure monocrystalline silicon and that of less perfect poly-

crystalline samples, we have been unable to detect any significant deviation in the optical absorption and reflectivity of our multicrystalline silicon ribbon material, with very high oxygen content, from that of monocrystalline silicon, in the wavelength range from 800 to 1200 nm. Our data are consistent, within the experimental accuracy, with those compiled by Green [1] for pure monocrystalline silicon.

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