Polarized Raman Spectroscopy and Chemometric Analysis of Micro-crystalline Silicon for Solar Cells

David Adley[1,a], Tatiana S. Perova[1,2,b], Eamonn Monaghan[3,c], and A.R. Ellingboe[3,d]

[1]*Department of Electronic and Electrical Engineering, Trinity College Dublin, Ireland*

[2]*ITMO University, St.-Petersburg, Russia*

[3]*School of Physical Sciences, Dublin City University, Ireland*

Abstract. Micro-crystalline silicon (μc-Si:H) is currently under extensive investigation due to it's applications in solar cells. The crystalline content and structural properties of μc-Si:H can be determined from several characterisation techniques such as high-resolution transmission electron microscopy (HRTEM), X-Ray diffraction (XRD), spectroscopic ellipsometry (SE) and Raman spectroscopy. In this paper a solution is proposed to reduce the effect of second order phonons on the Raman spectra of μc-Si:H for evaluation of crystalline volume fraction χ_c.

1 Introduction

Hydrogenated microcrystalline Silicon (μc-Si:H), consists of small crystalline grains embedded in an amorphous matrix. It has a higher doping efficiency requiring less Hydrogen than amorphous hydrogenated Si (a-Si:H) so is resistant to the Staebler-Wronski effect and has increased absorption efficiency at longer wavelengths than a-Si:H [1]. It has strong potential in multijunction solar cells. Multijuction cells consist of layers of a-Si:H and μc-Si:H sandwiched together using their different absorption characteristics to capture as much of the incident light spectrum as possible. VHF-PECVD has been shown to produce high quality crystalline material at high deposition rate [2]. Since the optical and electrical properties of μc-Si:H depend on the fraction of crystalline material, the crystallite size, and the grain boundaries an accurate determination of the crystalline volume fraction for μc-Si:H is of primary importance. Polarized micro-Raman spectroscopy and Chemometric analysis of Raman spectra of numerous samples of μc-Si:H were employed in this paper in order to determine the more reliable technique for sample characterisation.

2 Experimental

2.1 Sample fabrication

A large selection of μc-Si:H samples deposited on glass substrates by VHE-PECVD (30-300 MHz) having varying crystalline volume fractions were used as a sample set. This set of samples covering the complete crystallinity spectrum were manufactured by adjusting the silane and hydrogen ratio during μc-Si:H film deposition (see Ref.[2] for details).

2.2 Characterisation

Raman spectra were registered in a backscattering geometry from the samples using a RENISHAW 1000 micro-Raman system under 514 nm (Ar+ laser) and 633 nm (He-Ne laser) excitations. The use of different excitation wavelengths allows the Raman signal to be collected at different depths of penetration.

3 Results and discussion

The examples of Raman spectra registered from μc-Si:H samples with different χ_c values are shown in Fig. 1 (a). It can be seen that these Raman spectra composed of a sharp peak centred at ~520 cm^{-1}, assigned to the microcrystalline part of the film, and of a broad band around ~485 cm^{-1}, attributed to the amorphous Si phase. The crystalline volume fraction, χ_c is normally determined as the ratio of the integrated intensities of LO Raman band of crystalline Si at ~ 520 cm^{-1} and the TO band of amorphous Si (a-Si) at 485 cm^{-1}. As these bands overlap several techniques have been developed to deconvolute the spectra into its separate components, using typically two and three peaks fitting. Two peaks fitting assigns one Gaussian peak to the amorphous component and a second Lorentzian peak to the crystalline component of the μc-Si:H spectrum. Furthermore, the amorphous

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[a]adleyd@tcd.ie, [b]perovat@tcd.ie, [c]bjorn.mt@gmail.com, [d]bert.ellingboe@dcu.ie

component is not represented by a single Gaussian function but rather a combination of optical and acoustic phonon bands [3], therefore the Gaussian function does not adequately fit the spectra without significant error. Adding a further peak, intermediate between the amorphous peak and the crystalline peak as shown in Fig. 1(b), significantly reduces the residual error, however there is little evidence of a physical explanation to account for this additional peak [4].

If three peaks fitting is used the χ_c is then determined from Eq. (1)

$$\chi_c = (I_c + I_m)/(I_a + I_m + \gamma I_c),$$

(1)

where I_a, I_m and I_c are the amorphous, intermediate and crystalline Raman integrated intensities, and γ is a wavelength dependent scaling factor taken to be on average 0.88 [3]. It is extremely difficult to reliably and repeatably fit the amorphous and intermediate peaks. Smit et al. [3] proposed an alternative technique in which the shape of the amorphous component was considered constant across samples of varying crystallinity and the change in the spectra was primarily due to changes in the crystalline peak. All peaks surrounding the first order scattering between approximately 200 and 440 cm^{-1} are assigned to the amorphous spectrum. A 'least squares fit' was then applied in order to scale a reference amorphous spectra so that it could then be subtracted from the sample spectra.

The remaining spectra could be assigned to the microcrystalline component. The crystalline volume fraction was then found as

$$\chi_c = I_c/(I_a + \gamma I_c),$$

(2)

where I_c is the integrated intensity of the spectrum remaining after the amorphous component subtraction, this corresponds to the microcrystalline component. I_a is the TO component of the amorphous spectrum, the TO component can be found approximately by fitting with three Gaussian curves (see [3] for details).

This was significantly more reliable than the two and three peaks fitting approaches. However this technique suffers from several problems. The crystalline component does not consist solely of the first order Raman peak at approximately 520 cm^{-1} but also includes second order peaks of Raman scattering including overtone, combination and acoustic phonon peaks at wavenumbers above and below the central TO peak at ~520 cm^{-1} [5]. The influence of these second order peaks is more pronounced for longer wavelengths of excitation such as 633 nm due to its larger penetration depth. As these peaks result from the crystalline phase, they are most pronounced when the sample has a large crystalline component. The second order peaks overlap the regions assigned purely to the amorphous spectra and used to calculate the scaling factor in [3]. Therefore

the correct scaling factor cannot be found using the least fit analysis described in [3] due to this overlap and leading to errors as shown in Fig. 2 (a).

(a)

(b)
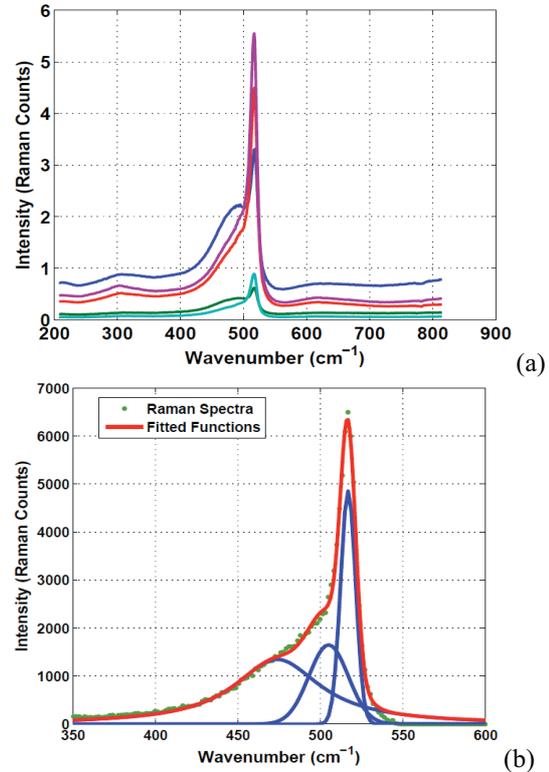
Figure 1. a) Raman spectra of investigated µc-Si:H sample with different crystalline volume fraction, b) example of fitting of Raman spectrum with 2 Gaussian and 1 Lorentzian functions (three peaks fitting).

In order to find the correct multiplier or scaling factor for spectra subtraction, the crystalline second order phonon peaks must be suppressed or removed. In single crystal Si the contribution of the acoustical phonons can be substantially suppressed by using polarized Raman measurements in VH or [001(100,010)00-1] geometry (see [6] for details). However, in µc-Si:H with a very high crystalline volume fraction, a much reduced second order spectrum was still visible despite attenuating polarisation filters, particularly in the region at 300cm^{-1}. At the same time the amorphous peak at 630 cm^{-1} does not have this problem. Therefore, this peak was used to obtain the scaling factor. The a-Si spectrum is then scaled by this factor and subtracted from the microcrystalline Si spectrum as shown in Fig. 2 (b). Table 1 shows the results of the crystalline volume fraction χ_c calculations using different fitting techniques discussed above. It can be seen from the Table 1 that the two peaks fitting results in significantly smaller χ_c values than obtained from the other techniques in particular for the larger χ_c. The fitting using the 630 cm^{-1} peak shows a higher χ_c value in general than the other columns as it is less effected by the contribution from the second order Raman peaks which tend to promote low crystallinity values. This technique can also be applied using

non-polarised light to improve the resolution of the Smit's [3] approach.
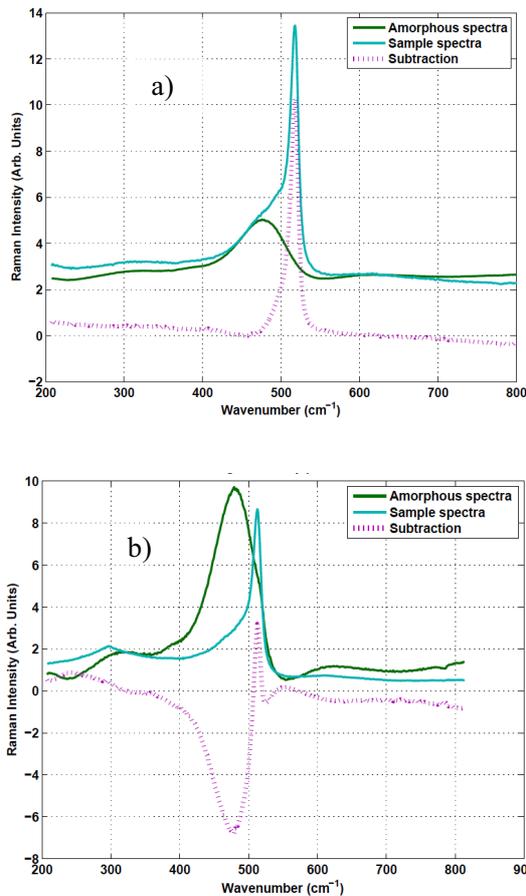
An alternative technique is to use regression analysis in particular Classical Least Squares (CLS) to determine the scaling factor. The CLS model assumes that measurements are the weighted sum of linearly independent signals. In spectroscopy, the CLS model assumes that measured spectra are the sum of pure component spectra weighted by their respective concentration. Thus, the model is $x=pS$, where x is the measured spectra, S is the matrix of pure component or basis spectra and p is the vector containing the concentrations of the component spectra or loadings. Generally, given the vector of measurements, x, one would like to know p, the degree to which each component contributes to the overall measurement. Of the chemometric techniques tested this was found to be among the simplest and best. The Eigenvector PLS Toolbox [7] was used for CLS fitting. Initially the dataset was pre-processed using SavGol smoothing, second order polynomial baseline fitting, and area normalisation. The scaling factor for each individual µc-Si:H spectrum is found in the loading matrix (p) consisting of two factors corresponding to the amorphous and crystalline components. The amorphous factor can then be used as the scaling factor in the technique described in [3]. Table 2 displays the results of this approach.

Table 1. Calculations of χ_c values using Eqs. (1) and (2) and Smit's [3] approach.

Table 2. Calculations of χ_c values using CLS approach.

Sample Name	Fitting with		Smit's approach		Sample Name	CLS	Smit's model, 630 cm^{-1}	Two peaks fit
	2 peaks	3peaks	630 cm^{-1} peak	both peaks				
S1	0.41	0.57	0.71	0.70	S11	0.36	0.48	0.37
S2	0.42	0.59	0.68	0.67	S12	0.25	0.35	0.26
S3	0.20	0.40	0.28	0.32	S13	0.20	0.28	0.24
S4	0.35	0.52	0.63	0.60	S14	0.15	0.24	0.18
S5	0.27	0.45	0.53	0.48	S15	0.12	0.18	0.13
S6	0.44	0.59	0.72	0.68	S16	0.09	0.14	0.10
S7	0.47	0.60	0.46	0.46	S17	0.04	0.12	0.09
S8	0.21	0.43	0.45	0.44	S18	0.02	0.08	0.07

cm^{-1} is used to determine the scaling factor then the CLS method should provide the best results.

4 Summary

Both the polarisation and chemometric techniques significantly attenuates the influence of the second order phonons and enables for more accurate calculation of the crystalline volume fraction for highly crystalline samples. The chemometric technique requires significantly shorter exposure time and could potentially be used to rapidly map large regions of the sample under investigation. If the sample is highly crystalline and only the phonon at 630

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