Determining the material structure of microcrystalline silicon from Raman spectra

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An easy and reliable method to extract the crystalline fractions in microcrystalline films is proposed. The method is shown to overcome, in a natural way, the inconsistencies that arise from the regular peak fitting routines. We subtract a scaled Raman spectrum that was obtained from an amorphous silicon film from the Raman spectrum of the microcrystalline silicon film. This subtraction leaves us with the Raman spectrum of the crystalline part of the microcrystalline film and the crystalline fraction can be determined. We apply this method to a series of samples covering the transition regime from amorphous to microcrystalline silicon. The crystalline fractions show good agreement with x-ray diffraction results, in contrast to crystalline fractions obtained by the fitting of Gaussian line profiles applied to the same Raman spectra. The spectral line shape of the crystalline contribution to the Raman spectrum shows a clear asymmetry, an observation in agreement with model calculations reported previously. The varying width of this asymmetrical peak is shown to correlate with the mean crystallite size as determined from XRD spectra. © 2003 American Institute of Physics. [DOI: 10.1063/1.1596364]

I. INTRODUCTION

Hydrogenated amorphous silicon (a-Si:H) has been studied for application in solar cells for several decades. Nowadays, microcrystalline silicon (μc-Si:H) also receives much attention because it is a suitable material for application as the intrinsic layer in the bottom cell of thin-film tandem solar cells. To study the material properties, the complete set of analysis techniques used in a-Si:H research (reflection/transmission spectroscopy, subgap absorption, dark and photocconductivity, etc.) can be copied, although carefully. In addition, the study of this material should also include the determination of the crystalline fraction, because μc-Si:H silicon is a heterogeneous material and consists of crystalline and amorphous regions. The fraction of crystalline material, the crystallite size, and the grain boundaries have an important influence on the optical and electrical properties that are relevant for application in solar cells. Void and grain boundaries, for example, could contain a high density of recombination centers, whereas a high crystalline fraction is likely to increase the mobility of the charge carriers.

Four techniques are commonly used to analyze the structural properties of μc-Si:H: high-resolution transmission electron microscopy (HRTEM), x-ray diffraction (XRD), spectroscopic ellipsometry (SE), and Raman spectroscopy. However, none of these techniques leads to an unambiguous determination of the crystalline fraction in μc-Si:H films. First, HRTEM is a complicated technique and its respective images have a poor contrast on amorphous material, so regions where amorphous and crystalline material overlap in the sample will appear to be fully crystalline in the two-dimensional image. Therefore, it is difficult to determine the crystalline fraction in microcrystalline material from these images, whereas the crystalline fraction is so small (smaller than a few percent) that the crystals do not overlap in the image. Particle sizes, though, can be extracted. Second, XRD is an easier technique, but a reasonable scan takes at least 2 h for films of about 500 nm thick. Also, it is not straightforward to extract the crystalline fraction, although some researchers reported doing so. The average particle size can be extracted from the XRD peak widths. Third, SE is a
simple and easy measurement technique. It gives the dielec-
trical constant as a function of energy, which is fitted with a
model containing parameters like film thickness and crys-
talline and void fractions. However, it is not unambiguous as
to which model is accurate and realistic.

A fourth technique to analyze the structural properties is
Raman spectroscopy. Most methods used in literature to ob-
tain crystalline fractions from Raman spectra are based on
peak fitting and suffer from interpretation problems. For ex-
ample, often, three peaks instead of two (one for the crystal-
line and one for amorphous part) are necessary to fit the
experimental data. The need for three peaks is often ex-
plained by introducing an extra phase in the material. Fur-
thermore, the crystalline fractions that result from peak fit-
ting are very sensitive to the choice of input parameters, like
whether peak positions are allowed to vary and the range of
data points that is included in the fitting procedure.

In this article, we will first review reported methods to
obtain information on the material structure from Raman
spectra. Then, we propose an alternative approach to separate
the amorphous and the crystalline contributions to the Ra-
man spectrum of the microcrystalline silicon film that is to
be examined. This method is applied to a series of silicon
films that covers the transition from amorphous to micro-
crystalline. We will show that this technique automatically
resolves several problems related to the methods used in lit-
erature. Finally, we shall compare crystalline fractions ob-
tained with this method with results from XRD analysis and
Gaussian line profile fitting procedures on the same samples
and present our conclusions.

II. RAMAN SPECTRUM OF MICROCRYSTALLINE
SILICON

A. The Raman spectrum

In a solid, a small part of the energy of an incoming
photon can be used to excite a lattice vibration (phonon). The
remaining energy escapes as a photon with a slightly smaller
energy compared to the incoming photon. This energy shift
is denoted as a Raman shift. In a crystalline solid, the mo-
mentum conservation law selects only phonons with zero
momentum, because the momentum of the photon is negli-
gibly small. In monocrystalline silicon, only the optical pho-
non with energy 64 meV has zero momentum and this leads
to the sharp peak at a Raman shift of 520 cm$^{-1}$ [Fig. 1(a)]. In
$\alpha$-Si:H, the momentum selection rule is relaxed and a variety
of phonon modes and energies are allowed. A broad peak
centered at 480 cm$^{-1}$ now dominates the Raman spectrum
[Fig. 1(b)]. $\mu c$-Si:H can be considered as a mix of crystal-
line Si ($c$-Si) and $\alpha$-Si:H. The Raman spectrum, however, is
not simply the sum of a monocrystalline silicon and an am-
orphous silicon spectrum, as can be seen in Fig. 1(c). This is
due to the fact that the Raman spectrum of a small crystallite
is different from a Raman spectrum of monocrystalline si-
clon. It is not straightforward how to determine which part of
the spectrum is due to the crystalline fraction and which part
can be attributed to the amorphous fraction in $\mu c$-Si:H. This
determination is necessary, though, in order to extract the
crystalline fraction from Raman spectra.

B. Ways to get the material structure from Raman
spectroscopy

We will first shortly review several techniques that have
been reported to separate the Raman spectra into a crystalline
and an amorphous contribution. The simplest way is just to
compare the peak height at 520 cm$^{-1}$ to the peak height at
480 cm$^{-1}$ (e.g., see Ref. 6). This comparison gives only a
very rough estimate of the crystallinity of the material. Peak
fitting is more frequently used to unravel the spectrum. For
example, two peaks (Gaussian or Lorentzian line profiles)
can be used, one to describe the crystalline part and one for
the amorphous part, but this procedure does not lead to a
good fit to the measured Raman spectrum. Furthermore, the
low-energy peak, which is attributed to the amorphous frac-
tion, tends to shift to higher energies than the expected
480 cm$^{-1}$. As we will show later, this shift is not due to a
shift of the amorphous transverse optical (TO) phonon en-
ergy, but to the change in the Raman peak shape of the crys-
talline fraction. In order to obtain a good fit to the measured
spectra, at least three peaks are necessary. The third peak is
then attributed to surface modes or to hexagonal ordered
silicon.

The peak fitting routines described herein require this
extra peak because the peak shape of the crystalline part is
asymmetric and varies for different samples. As calculated
by Richter et al. and Campbell et al., the crystalline peak
width and position is influenced by the crystallite size and
shape. For example, calculations show that this peak be-
comes more and more asymmetric for smaller crystallite
sizes. Touri et al. account for this by using two asymmetri-
cal Lorentzian line profiles to obtain a good fit to their spec-
tra. They find peaks around 500 cm$^{-1}$ and 520 cm$^{-1}$ (and so
do we with our samples as we will show in Sec. IV D),
which they attribute to two distinct crystallite sizes. How-

FIG. 1. (a) Raman spectrum of monocrystalline silicon. (b) Raman spectrum of $\alpha$-Si:H. (c) Summation of (a) and (b) (solid line), scaled before summation by the eye so that the peak and the “bump” in (c) fit the peak and the “tail” of the Raman spectrum of $\mu c$-Si:H (dashed line).
observe this apparent peak shift in the Raman spectrum of a secondary phase in the amorphous material. We also strongly suggest that the Raman spectrum of the amorphous fraction in the energy region of the crystalline feature have an influence on the microcrystalline Raman transverse acoustic phonon mode of the amorphous film. The advantage is that in the unravelling of the Raman spectrum of \( \mu c \)-Si:H, not only the TO phonon mode of the amorphous component, is taken into account but also the other phonon modes. After the substraction, changes in the peak shape of the crystalline contribution to the Raman spectrum of \( \mu c \)-Si:H become clearly visible. The apparent peak shift shown in Fig. 2 can now be explained in a natural way as illustrated in the inset of Fig. 2: When the TO phonon peak in the Raman spectrum of an \( a \)-Si:H film is added to the asymmetrical sloped shoulder of the Raman peak of the crystalline fraction in \( \mu c \)-Si:H, then the position of the peak in the resulting line shape is expected to shift.

### III. EXPERIMENT

We deposited two series of silicon films of about 600 nm thick on Corning glass C1737 and \([100]\) oriented, slightly \( n \)-type, \( c \)-Si substrates simultaneously, using expanding thermal plasma chemical vapor deposition. Details on the deposition setup are reported elsewhere. The first series of samples is deposited using an \( \text{Ar} \) flow of 1200 sccm, a \( \text{H}_2 \) flow of 600 sccm, and a varying \( \text{SiH}_4 \) flow from 0.5 to 10 sccm. The second series is deposited using a constant \( \text{SiH}_4 \) flow of 5 sccm and a varying hydrogen flow. The argon flow was set at twice the hydrogen flow. A third series of samples is deposited using a pure \( \text{H}_2 \) plasma with a \( \text{H}_2 \) flow of 2000 sccm and a varying \( \text{SiH}_4 \) flow on glass and Al foil and the films are about 5000 nm thick.

The Raman spectra of the silicon films on the glass substrates are measured using a Raman microscope (Renishaw- Gloucestershire, UK) Ramascope system 2000, grating 1800 lines/mm) in a backscattering geometry with a 2 mW Ar laser at a wavelength of 514.5 nm focused in a spot of about 1 \( \mu m \). On the samples on \( c \)-Si substrates of the third sample series, one XRD measurement is carried out (Bruker–Nonius (Delft, The Netherlands) D5005 \( \theta / \theta \) diffractometer with diffracted beam graphite monochromator, wavelength Cu \( K \alpha \)). On these samples three with Al substrates, XRD measurements are also carried out to determine the crystalline fraction.
the TO phonon peak means that the residue in the regions in the spectrum outside peaks at the amorphous acoustical phonon energies. That 440 cm$^2$~ the amorphous and in the microcrystalline spectra low-energy side of the TO crystalline peak at 520 cm$^2$.

IV. RESULTS AND DISCUSSION

A. Splitting a Raman spectrum into a crystalline and an amorphous contribution

In order to split the Raman spectrum of a $\mu$c-Si:H film into a crystalline and an amorphous contribution, we subtract a scaled Raman spectrum of an a-Si:H film (Fig. 4). The result is denoted as $\mu$c-Si:H$-A\times$ a-Si:H$-B$, where $B$ is a flat background to correct for the dark counts and background light. Because of differences in signal strength (caused by differences in sample alignment and film composition) the amorphous spectrum is scaled by factor $A$ before subtraction. The values for this constant and background are obtained in a least-squares routine, realizing that the crystalline contribution to the spectrum of $\mu$c-Si:H cannot contain peaks at the amorphous acoustical phonon energies. That means that the residue in the regions in the spectrum outside the TO phonon peak (we take the region 200 cm$^{-1}$ to 440 cm$^{-1}$ and 560 cm$^{-1}$ to 850 cm$^{-1}$) should be minimized.

The resulting crystalline part of the spectrum shows a flat background, as can be seen in Fig. 4. The features at the low-energy side of the TO crystalline peak at 520 cm$^{-1}$ in the amorphous and in the microcrystalline spectra (in the energy range of 150 cm$^{-1}$ to 480 cm$^{-1}$) that are attributed to the LA, TA, and LO amorphous phonon modes are absent. Moreover, the broad features at the high-energy side in the amorphous and microcrystalline spectra at about 650 cm$^{-1}$ and 950 cm$^{-1}$, which are attributed to two-phonon excitations in a-Si:H and to the Si–H wagging mode, are also subtracted correctly. The only feature that remains is a bump at 960 cm$^{-1}$. This feature is due to the two-phonon excitation process in c-Si (it can also be noticed in the Raman spectrum of $\mu$c-Si:H in Fig. 4) and should therefore be present in the Raman spectrum of the crystalline fraction. These observations strongly suggest that the procedure followed splits the Raman spectrum of $\mu$c-Si:H into the amorphous and the crystalline contributions. The small uncorrelated residue that is obtained after the subtraction is strong evidence for the assumption that the shape of the Raman spectrum of a-Si:H used in this procedure is the same as the shape of the Raman spectrum of the amorphous fraction in $\mu$c-Si:H.

B. Raman spectrum of the crystalline fraction

In Fig. 5, the XRD measurements of the first sample series (see Sec. III) are presented and it can be concluded that the samples deposited with SiH$_4$ flows from 0.5 to 5 sccm contain a crystalline fraction and the sample deposited with a SiH$_4$ flow of 10 sccm does not. The Raman spectra of the silicon films are split into an amorphous and a crystalline contribution following the procedure just described. The crystalline part of the Raman spectra is shown in Fig. 6. The spectra are normalized to the maximum of the Raman peak. For comparison, the Raman spectrum of $\mu$c-Si:H is also shown in Fig. 6. Clearly, the peak of the crystalline fraction in $\mu$c-Si:H is broader than the microcrystalline peak. It also clearly shows an asymmetry. Richter et al.$^5$ calculated the Raman spectrum of a finite-sized spherical silicon crystal and found a similar asymmetry. With smaller particle size, the momentum selection rule of the Raman process is more relaxed. With increasing momentum, the TO phonon energy becomes lower, so when a momentum greater than zero is
allowed, lower-energy phonons will be excited. This leads to a broadening of the Raman peak toward the low-energy side, resulting in an asymmetrical peak shape.

The calculations of Richter et al. explain the asymmetry, and revealed that the broadening depends on crystallite size. Figure 6 shows that the broadening increases with increasing silane flow. The average particle size is determined from the XRD measurements by applying the Scherrer equation to the integral width of the peak that corresponds to the [220] lattice planes. Although they use the full width half maximum (FWHM) of a fitted symmetrical Lorentzian line shape. Calculations of Campbell et al. show a similar trend. It should be realized that the calculations concern Raman scattering on a ball-shaped particle having a specific size, while a distribution of particle sizes, maybe with different shapes, contributes to the experimental data. Also, calculated data of Richter et al. are shown, but they show a large deviation from the other data in Fig. 7.

C. Determining the crystalline fraction

The peak areas of the crystalline and the amorphous parts of the Raman spectra correlate to the amount of c-Si and a-Si:H in the film. It is not possible to obtain absolute values because the detection efficiency is usually not known. The ratio of the two peak areas, however, corresponds to the ratio of the amount of crystalline to the amount of amorphous silicon. This ratio needs to be corrected for the difference in the cross sections for phonon excitation of c-Si compared to that of a-Si:H. For the TO phonon, the ratio of these two cross sections \( \sigma_{cSi}/\sigma_{aSi:H} \) is usually set at 0.8. It should be noted that this cross section ratio is reported to depend on the crystallite size, and varies from about 0.9 to about 0.7 as the crystallite size ranges from 5 to 15 nm, which are typical sizes for our samples. Now, we have to determine which part of the amorphous spectrum that is subtracted is due to the TO phonon excitation. In Fig. 8, the contributions of the four phonon modes are fitted to the amorphous spectrum using four Gaussian line profiles and the peak area of the TO phonon Raman scattering is used in the calculation of the amorphous fraction in the microcrystalline films.

FIG. 7. The FWHM is displayed versus the average particle size as obtained from XRD measurements. Also, other reported data, experimental as well as calculated, are presented for comparison. The data point completely on the right-hand side of the reciprocal x axis is measured on an “infinitely” large c-Si wafer.

FIG. 8. Four Gaussian line profiles (dashed lines) are fitted to a Raman spectrum of a-Si:H to obtain the contribution of the TA, LA, LO, and TO phonon modes. The peak area of the TO phonon is used in the calculation of the amorphous fraction in the microcrystalline films.

FIG. 9. The crystalline fraction versus the hydrogen flow used during deposition.

TABLE I. Crystalline fraction (%) determined from XRD and from Raman spectra using different techniques. The crystalline fractions determined from the Raman spectra are calculated using [cryst]/([cryst] + 0.8[am]). First column: Silane flow. Second column: Crystalline fractions from XRD. Third column: Crystalline fraction determined as described in this article. Fourth column: For [cryst] and [am], the Raman intensities at 520 cm$^{-1}$ and 480 cm$^{-1}$, respectively, are taken. Fifth column: Fitting of three Gaussian line profiles as described in Refs. 2 and 20. Sixth column: Fitting of five Gaussian line profiles as described in Refs. 10 and 21. From a sample deposited with a silane flow of 18 sccm, no crystalline fraction was detected with all techniques.

<table>
<thead>
<tr>
<th>SiH$_4$ flow (sccm)</th>
<th>XRD</th>
<th>Raman [480] versus [520]</th>
<th>Raman (3 Gauss)</th>
<th>Raman (5 Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>58±9 52±4</td>
<td>72±4</td>
<td>46±10</td>
<td>38±6</td>
</tr>
<tr>
<td>14</td>
<td>50±6 46±4</td>
<td>69±3</td>
<td>40±17</td>
<td>31±6</td>
</tr>
<tr>
<td>16</td>
<td>12±2 11±4</td>
<td>46±2</td>
<td>3±1.5</td>
<td>5.3±2.5</td>
</tr>
</tbody>
</table>

Note: cryst indicates crystalline and am indicates amorphous.

aSee Ref. 3.

bSee Ref. 6.

determined from XRD measurements and from Raman spectra using different techniques. The crystalline fractions determined from the Raman spectra are calculated using [cryst]/([cryst] + 0.8[am]). First column: Silane flow. Second column: Crystalline fractions from XRD. Third column: Crystalline fraction determined as described in this article. Fourth column: For [cryst] and [am], the Raman intensities at 520 cm$^{-1}$ and 480 cm$^{-1}$, respectively, are taken. Fifth column: Fitting of three Gaussian line profiles as described in Refs. 2 and 20. Sixth column: Fitting of five Gaussian line profiles as described in Refs. 10 and 21. From a sample deposited with a silane flow of 18 sccm, no crystalline fraction was detected with all techniques.

that a minimum of 10% to 20% of the amorphous material is characteristic for the deposition conditions used in this article.

D. Comparison with other techniques

To validate the method described herein to obtain crystalline fractions, the crystalline fractions of the third series of samples (see Sec. III) are determined from XRD measurements, using the method described by Williamson. The data are determined from XRD measurements and from Raman spectra using different techniques. The crystalline fractions determined from the Raman spectra are calculated using [cryst]/([cryst] + 0.8[am]). First column: Silane flow. Second column: Crystalline fractions from XRD. Third column: Crystalline fraction determined as described in this article. Fourth column: For [cryst] and [am], the Raman intensities at 520 cm$^{-1}$ and 480 cm$^{-1}$, respectively, are taken. Fifth column: Fitting of three Gaussian line profiles as described in Refs. 2 and 20. Sixth column: Fitting of five Gaussian line profiles as described in Refs. 10 and 21. From a sample deposited with a silane flow of 18 sccm, no crystalline fraction was detected with all techniques.

FIG. 10. Several fitting techniques that are described in literature, applied to a typical Raman spectrum of microcrystalline silicon. (a) Three Gaussian line profiles (see Refs. 2 and 20), (b) Five Gaussian line profiles (see Refs. 10 and 21), and (c) Two asymmetrical Lorentzian line profiles (see Ref. 9).
results. Crystalline fractions obtained with peak fitting techniques that are presented in literature do not agree as well with the XRD results. The method presented here is not sensitive to the range of data points that is included. Furthermore, it is straightforward what part should be attributed to the crystalline, and what part to the amorphous part of the spectrum. And finally, there is no discussion about peak positions that should be fixed or not to obtain realistic results. These are clear advantages above peak fitting methods. The earlier reported discrepancy (Refs. 2 and 22) in the crystalline fractions obtained from XRD and Raman spectroscopy is not observed in our samples when the subtraction method described in this article is applied to the Raman spectra.

V. CONCLUSION

We have demonstrated an alternative technique to extract the structural composition of μc-Si:H from Raman spectroscopy. Crystalline fractions obtained using this technique show good agreement with fractions obtained from XRD analysis, in contrast to crystalline fractions obtained by frequently used fitting procedures in literature. Furthermore, the subtraction of the amorphous part of the spectrum (taken from a Raman spectrum of an a-Si:H film) clearly reveals the asymmetrical peak shape of the Raman spectrum of the crystalline fraction as calculated in literature. Interpretation difficulties arising from peak fitting are resolved in a natural way.

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20. Since not all information is available, all Gaussian line profile parameters were free to vary and we included the data in the range 400 cm⁻¹ to 550 cm⁻¹ in the fitting procedure.
21. The data range that is included in the fitting procedure is not mentioned, so we took the range of 400 cm⁻¹ to 550 cm⁻¹ in the fitting procedure.