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Dopant mapping in highly p-doped silicon by micro-Raman spectroscopy at various injection levels

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Micro-Raman spectroscopy has been used to investigate the acceptor distribution in highly p-doped silicon. As an example, the dopant distribution in crystalline thin-film layers, as developed for solar cells, was mapped. The method is based on the analysis of the Fano-type Raman peak shape which is caused by free charge carriers. For calibration of the Raman acceptor measurements (excitation at a wavelength of 532 nm), we used mono-crystalline reference samples whose acceptor concentration was determined by electrochemical capacitance voltage. We find a significant influence of light induced free charge carriers on the peak shape which results from typical Raman excitation. Thus, the selection of a suitable intensity is important to avoid a too low signal-to-noise ratio on the one hand and systematic errors due to light induced carriers on the other hand. Different evaluation methods, i.e., peak asymmetry versus peak width analysis, are compared in respect to interference caused by random noise of the spectra or else by internal stress in the sample. While the width analysis method is more robust to a low signal-to-noise ratio, the symmetry analysis is more reliable in case of high intrinsic stress. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4773110>]

I. INTRODUCTION

Highly p-doped regions are present in most types of silicon solar cells, as they are used as back surface fields at otherwise recombination active interfaces and moreover facilitate the formation of efficient electric contacts.¹ An interesting method for spatially resolved investigation of such regions is micro-Raman spectroscopy. It can reveal intrinsic stress, which may be related, e.g., to the specific processing of such regions.² Recently, it has been shown that μ -Raman is also suitable to study the spatial dopant distribution in such regions.³ The method is based on the analysis of the Raman peak shape, which is correlated to the kind and concentration of free charge carriers. Advantages in comparison to other methods such as electrochemical capacitance voltage (ECV)⁴ are the high lateral spatial resolution and its suitability to non-standard samples with, e.g., high surface roughness.

Examples for such non-standard samples are crystalline silicon thin-film layers on foreign (i.e., non-silicon) substrates. Such systems offer an interesting alternative to the widely used silicon wafer solar cells, because such solar cells can be directly fabricated by large-area deposition, and only a fraction of the usual amount of high purity silicon is necessary.⁵

Dopant mapping by Raman is a relatively new method. Therefore, a precise calibration with samples at various well-known doping levels is necessary. It has been shown that the excitation wavelength plays a crucial role.⁶ After such a cali-

bration is established for a frequent laser type, it can also be used for other Raman systems of this type without further calibration. Furthermore important is the study of robustness of the method and interferences with other effects. Intrinsic stress of the samples is such an effect, which is also known to influence the peak shape. Also, the intense illumination by the Raman excitation itself results in additionally induced free charge carriers, which may affect the validity of the results. Even the Raman illumination related local heat creation has been debated as a source for peak deformation.⁷

In this work, we investigate cross sections of silicon layer systems, as developed for crystalline thin-film solar cells, by μ -Raman spectroscopy mappings. A calibration for hole concentration measurements by Raman systems with widely used 532 nm lasers is established. For this purpose, we use mono-crystalline reference samples, whose acceptor concentration has been determined by ECV. Different influences, which are likely to interfere with the measurements, such as different injection levels imposed by the source laser or intrinsic stress of the samples are studied. Apart from the symmetry (Fano) parameter, also the width of the peaks is investigated for data evaluation.

II. THEORY

A. Raman spectra

The Raman spectrum has one peak for unstrained silicon. This peak is related to the triple degenerated optical phonon mode at 521 cm^{-1} . Due to the cubic symmetry, only the peak intensity but not the peak position depends on crystal orientation. In case of strained silicon, the degeneracy is

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broken. In practice, however, the peaks cannot be individually resolved, and thus both shift and broadening of the peak are observed.

For exact quantitative evaluation of the stress from the peak shift, the exact crystal orientation has to be known. If this is not the case, an evaluation with reasonable precision can be calculated from the value at (100) orientation by⁸

$$\varepsilon = -250 \text{ MPa} \cdot \text{cm} \cdot \Delta k \quad (1)$$

(ε : mean stress of the in-plane components, Δk : peak shift with respect to non-stressed sample). That is a positive peak shift which indicates compressible stress.

B. Raman peak shape

In undoped silicon, the Raman peak shape can be described by a Lorentz (or Breit-Wigner) distribution

$$I(k) = A \cdot \frac{1}{1 + [2(k - k_{\text{Phonon}})/\Gamma]^2} \quad (2)$$

(Γ : width (full width at half maximum height), A : peak height, k : wave number) The peak maximum is at $k = k_{\text{Phonon}}$. One well-known broadening mechanism is temperature related⁷ and interpreted as being the result of decremented phonon decay time.

In highly doped silicon (about 10^{18} cm^{-3} or higher), the Raman peak shape is significantly influenced by the kind and concentration of free charge carriers. This influence of the peak shape on carrier concentration is explained by the coupling of the phonon (discrete state) with intraband transitions of the free carriers (continuum of states). The theory is described in detail in Refs. 3 and 6. Here, we only summarize the facts, which are necessary for interpretation of our data.

As result of the phonon-free carrier coupling in highly doped silicon, the Raman peak shape becomes asymmetric, which is described by the Fano distribution

$$I(k) = I_0 \frac{(q + 2(k - k_{\text{Phonon}})/\Gamma)^2}{1 + [2(k - k_{\text{Phonon}})/\Gamma]^2} \quad (3)$$

(I_0 : scaling factor, q : symmetry (or Fano) parameter). The absolute value of the inverse Fano parameter $1/q$ (i.e., degree of asymmetry) increases with the free carrier concentration. Its sign is positive for holes and negative for electrons. Comparing same free carrier concentrations, the effect is much stronger for holes than for electrons.⁹ In case of the Fano distribution, the peak maximum is not exactly at k_{Phonon} , but slightly shifted. The numerical values reported here always refer to k_{Phonon} , likewise for the shift Δk .

For low carrier concentration, the Fano distribution (3) approaches the Lorentz distribution (2), which can be seen by substituting $A = I_0 \cdot q^2$ and $q \rightarrow \infty$.

In case of holes, a linear relation to the carrier concentration c_h is found³

$$\frac{1}{q} = B \cdot c_h, \quad (4)$$

with the slope B strongly depending on the excitation wavelength. A further effect is an increased width as compared to intrinsic material. For the additional, free carrier induced width Γ_F^0 , the following relation is given for holes:⁶

$$\Gamma_F^0 = 2\eta^{5/3} \left(\frac{1}{q} \right)^{2/3}, \quad (5)$$

with η being essentially a constant. Note that in the original work,⁶ the purely carrier induced width Γ_F^0 and the total width Γ are not precisely distinguished. However, as $q^{-1} = 0$ for intrinsic material, it is clear that Γ_F^0 has to be filled into Eq. (5).

A further effect is a shift of the phonon wavenumber k_{Phonon} . This shift remains small (up to -0.4 cm^{-1} at c_h of $1.7 \times 10^{19} \text{ cm}^{-3}$) unless in case of very high doping.⁶

C. Consideration of different peak broadening mechanisms

In case of multiple relevant broadening mechanisms, a convolution of the respective distributions is obtained. For simultaneous broadening by Fano and Lorentz type, i.e., due to free carriers (resp. width Γ_F^0) and temperature (resp. width Γ_L), the resulting distribution is of Fano type and the new width Γ_F is simply a sum of the original ones³

$$\Gamma_F = \Gamma_F^0 + \Gamma_L. \quad (6)$$

By the measurement system itself, further broadening is introduced, which is typically a Gaussian distribution D_G . Thus, the distribution of the experimental spectra D_{GF} is not exactly of the Fano type and fitting of a Fano distribution will result in a systematic error. Both Raman and Raman peaks are subject to this, which can be used to get the system width Γ_G . By this, some kind of reversal convolution, to increase the precision, is obvious. On the other hand, numerical deconvolution of experimental data is known to amplify the noise; therefore in this work, two other options are used:

(I) The data are fitted by a convoluted distribution $D_G * D_F$ (* is the convolution operator). D_G is a unit-area Gauss distribution with the known system width and D_F the Fano distribution whose parameters are varied during fitting. The resulting width will be referred to as the “deconvoluted” width Γ_F . It should be independent of the acquisition system and facilitate comparison with the theory.

(II) The data are directly fitted by a Fano distribution. The obtained width Γ also depends on the (in our case constant) broadening of the measurement system. As will be confirmed by our results later on, only for the width the results of (I) and (II) differ significantly. Moreover, after calibrations both width values provide similar results for the dopant concentration. As the numeric calculation for this option is less costly, we have chosen it for mappings.

III. EXPERIMENTAL

A. Preparation of samples

1. Mono-crystalline samples for calibration

In order to find the exact relationship between dopant concentration and the Raman peak shape at various injection

levels, silicon layers at different doping levels were prepared by epitaxy on mono crystalline wafers. The layers were deposited by convection assisted chemical vapor deposition (CoCVD) in a large-area deposition system as described in Ref. 10. The silicon substrates were float-zone, 100 mm in diameter. The resulting layers have low stress, below the detection limit of Raman measurements. Their carrier concentration can be reliably determined by ECV measurements. Layers with different boron dopant concentration with a thickness of about 20 μm were fabricated. After growth, the substrates were divided, one part was used for ECV, another for Raman. For the Raman sample, about 1 μm was etched off by CP-4 polishing etchant prior to the measurement.

2. Samples for investigations of polycrystalline thin-films

The layer system investigated was nearly the same as the layers used for developing crystalline silicon thin-film solar cells.¹¹ The layers were deposited on high purity graphite ("FP479", Schunk Kohlenstofftechnik, Gießen, cf. also Ref. 12). The thermal expansion coefficient of the substrate, as specified by the supplier in the range of 20 to 1000 °C is $6.0 \times 10^{-6} \text{ K}^{-1}$. A SiC barrier layer grown at 1200 °C by CVD was used for sealing the pores of the substrate.¹²

Si layers of about 20 μm thickness were deposited on top of the SiC-layers by CoCVD. By boron doping, an acceptor concentration of $8 \times 10^{18} \text{ cm}^{-3}$ is obtained. In order to get a larger grain size in the mm-range, a zone melting recrystallisation (ZMR) process was applied. Balling up of liquid silicon was prevented by a thin capping layer of SiO_2 deposited before ZMR and removed after ZMR by wet chemical etching in HF solution. The resulting layers served as a seeding layer for subsequent epitaxial growth (cf. Ref. 13).

Two silicon epitaxial layers each with a thickness of about 20 μm and a boron doping concentration of $8 \times 10^{18} \text{ cm}^{-3}$ (first epitaxial layer) and $2 \times 10^{16} \text{ cm}^{-3}$ (second epitaxial layer) were grown by CoCVD. The growth of two subsequent epitaxial layers with different doping levels is different to our layer system used for solar cells. This structure has been chosen in this work in order to have a clear separation between growth method induced boundaries and doping level induced boundaries. A n-doped Si-layer was formed by spin on doping of a phosphorous solution and diffusion in a rapid thermal processing (RTP) furnace (cf. Ref. 14).

Further details of the layer processes were published in recent papers.^{5,15} From the layer structure, polished cuts of the cross sections were prepared.

B. Raman measurement setup and data evaluation

We used a micro-Raman equipment (alpha500 AR, manufactured by WITec GmbH). For excitation, a Nd:YAG laser at 532 nm was used, which results in a penetration depth in silicon of about 0.9 μm . The measured standard intensity was 2 or 5 mW (if not else explicitly mentioned), and in order to check for intensity related effects, additional measurements at 10 to 40 mW have been made for comparison. Spot size was in the range of 1 to 2 μm .

The samples were measured in backscattering geometry. The incident light was not polarized; also the detection setup contained no polarization filters. Sampling rate of the spectrometer is one measurement point at every 1.18 cm^{-1} . As the resolution is important in respect of evaluation of the peak width, we determined the spectral resolution of the spectrometer system by evaluation of the peak at $k=0$ (Raleigh peak). A Gaussian fit of this peak results in a peak width of 2.5 cm^{-1} . The laser beam was focused onto the sample by a 50 $\times$ objective at a numerical aperture of 0.75. Measurement time was in the range of 5 to 10 s for single point acquisition. In case of mappings, this time was greatly reduced to 83 ms per point. A mapping consists of 240×270 points.

For evaluation of the Raman spectra, direct fitting of the spectra by a Fano distribution was applied. This function is not supported by the supplier's measurement system; therefore all the spectra were exported and fitted by an adapted program developed for this purpose. Core of it is a numerical minimization based on Powell's conjugate gradient method, as published in Ref. 16.

As Eq. (3) contains the parameter q , which diverges for low doping concentrations, this equation is not suitable for numerical processing. We therefore modify the fitting function by substituting

$$p = \frac{1}{q} \text{ and } A = I_0 \cdot q^2 \quad (7)$$

(A corresponds to the peak height) and introducing the parameter y_0 for the detection baseline.

This results in a new function for fitting

$$I(k) = A \cdot \frac{(1 + 2p(k - k_{\text{Phonon}})/\Gamma)^2}{1 + [2(k - k_{\text{Phonon}})/\Gamma]^2} + y_0. \quad (8)$$

The fit is then obtained by minimising the mean square deviation to the spectrum in the interval $[480 \dots 560] \text{ cm}^{-1}$. Contrarily to function (3) for the modified function (8), automatic fitting of both highly and lowly doped regions can be applied. Even though a mapping contained 64 800 spectra, the fitting needed only a few minutes, which is negligible as compared to the measuring time of about 2 h.

As already described in Sec. IIC, for obtaining the deconvoluted width Γ_F , the distribution (Eq. (8)) is not directly used for fitting. Instead $I(k)$ is numerically convoluted by a unit-area Gauss function whose width is chosen alike the measured width of the Raleigh peak (i.e., 2.5 cm^{-1}).

C. ECV measurements

The electrochemical capacitance voltage method is used to determine the concentration profiles of thin structures, e.g., Refs. 17 and 18. For the ECV measurement, a WEP CVP21 profiler with a solution of $0.25 \text{ mol/dm}^3 \text{ NH}_4\text{F}$ is used.⁴ The electrochemical cell is based on the principle of Ambridge.¹⁹ An ohmic contact to the sample is realized with two probes. The concentration is calculated from the area A covered with the electrolyte (NH_4F) and bordered with a

sealing ring. The ring area A is 11 mm^2 . During the etch process of the semiconductor, the capacitance C versus voltage V is continuously measured. Assuming a sharp border of the sealing ring, that means a constant etch area and no undercutting among the sealing ring is observed,¹⁷ the concentration N can be calculated with the Mott-Schottky equation (9). The depth x is the sum of the etched depth (using the Faraday equation of electrolysis) and the depletion width (10)

$$N = \frac{-2}{e\epsilon_0\epsilon_R A^2 \frac{d(1/C^2)}{dV}}, \quad (9)$$

$$x = x_{\text{Etch}} + x_{\text{Depletion}} = N_{\text{Etch}} \cdot \Theta \cdot \frac{1}{A} + \frac{\epsilon_0\epsilon_R A}{C}, \quad (10)$$

N_{Etch} is the number of the etched molecules and Θ is the mean volume of one molecule per unit. ϵ_0 and ϵ_R are the vacuum permittivity and the dielectric constant of the semiconductor, respectively.

IV. RESULTS

A. ECV-measurements

A depth profile of the free hole concentration was made by ECV measurements for each of the fabricated mono-crystalline layers. Fig. 1 shows profiles of layers grown by 3 different recipes. Within the layers, the dopant concentration is quite uniform; however, close to the surface, the concentration suddenly drops. Such a decrease has already been observed for the growth of highly phosphorous doped epitaxial layers²⁰ and has been attributed to out-diffusion of dopant after the end of growth during cooling down. Therefore, in order to get high dopant uniformity within the Raman probed area, $1 \mu\text{m}$ of the surface was etched off from the Raman samples by applying a polishing etchant. The concentration averaged within the Raman excitation depth was used for the data evaluation (cf. Fig. 1).

B. Raman measurements at different doping levels

From another part of the grown layers, Raman measurements were made at an excitation power of 2 mW. A high

FIG. 1. Hole concentration profile obtained by ECV for epitaxial layers grown by 3 different recipes (no. 2, 3, 4). In order to get a uniform carrier concentration within the Raman excitation depth, $1 \mu\text{m}$ of the sample surface is etched off as indicated in the figure.

signal-to-noise ratio is obtained due to a long integration time of 5 to 10 s for a spectrum. In Fig. 2, such a single point spectrum is shown in comparison with typical spectra obtained from mappings, whereby the integration time was only 83 ms per spectrum, as they are described below. As obvious from the spectra scaled to the same peak height (Fig. 2(b)), the signal-to-noise ratio for single spectra is much lower.

Due to the free hole concentration, the spectra show a small but systematic asymmetry (Fig. 2(b)), which increases with increasing free carrier concentration.

Extraction of the Fano parameter, width Γ_F , and peak position was then obtained by fitting a convoluted distribution Fano*Gauss. Random errors of the obtained parameters, as estimated by repeated measurements, are small at this high signal to noise ratio. Error bars in the following diagrams are too small and therefore invisible.

In the next step, the inverse Fano parameter q^{-1} is plotted versus the hole concentration as obtained by ECV measurements (Fig. 3). As suggested by Eq. (4), a linear fit is applied

FIG. 2. Raman spectra of doped samples and fitted curves. The free holes result in an asymmetric deformation of the Lorentz peak, i.e., Fano shape. Fitted curves (lines) are Fano distributions convoluted by a Gaussian to account for the resolution of the measurement system. (a) Single point spectra (open squares) have higher count rates than spectra from mappings (filled circles) because of longer integration times. (b) Rescaling to identical peak height reveals the different signal to noise ratio. Resulting fit parameters are indicated in the legend.

FIG. 3. Fano parameter $1/q$ obtained by Raman point measurements (excitation power 2 mW) in dependence of hole concentration c_h by ECV of the respective layer. The line graph is a linear fit. Resulting fit parameters are indicated in the legend.

$$\frac{1}{q} = B \cdot c_h + p_0. \quad (11)$$

Fig. 3 shows that there is a good agreement to the linear fitting curve. A small offset p_0 is obtained which is further discussed below. The values of the parameters as obtained by the fit in Fig. 3 (and further) are shown in Table I.

The width Γ increases with the hole concentration similarly as the asymmetry parameter q^{-1} . To get the quantitative relation, the deconvoluted width (i.e., width compensated for the broadening due to the acquisition system) is plotted against the asymmetry parameter at the power of $2/3$, as suggested by Eq. (5). Fig. 4 shows a good agreement with the respective linear fit curve

$$\Gamma_F = 2\eta^{5/3} \left(\frac{1}{q} \right)^{2/3} + \Gamma_L. \quad (12)$$

According to Eq. (6), the obtained offset Γ_L at $q^{-1} = 0$ can be interpreted as the width in the absence of free carrier induced broadening, majorly due to measurement at room temperature. The obtained value for η of $4.69 \text{ cm}^{-3/5}$ is in good agreement with values published by Cerdeira *et al.*⁶ being between 5.0 and $7.0 \text{ cm}^{-3/5}$. Note that the small difference to the mean value may be due to the fact that most dopant values in this reference are much higher; moreover, other

TABLE I. Summary of values obtained by various fits.

Parameter	Eq. No.	Fig.	Comment	Value
B	(11)	3	Slope for Raman excitation at 532 nm	$2.41 \times 10^{-21} \text{ cm}^3$
p_0	(11)	3	Not 0, majorly due to finite excitation power	0.00232
Γ_L	(12)	4	Width of intrinsic Si at 0 mW excitation power at room temperature.	1.97 cm^{-1}
η	(12)	4	Also cf. Ref. 6	$4.69 \text{ cm}^{-3/5}$
E	—	5	Empirical fit: offset	3.79 cm^{-1}
F	—	5	Empirical fit: slope	$1.41 \times 10^{-19} \text{ cm}^2$

FIG. 4. Dependence of the deconvoluted width Γ_F (i.e., reduced by the Gaussian width contributed by the measuring system itself) on the Fano parameter. The line graph is a linear fit. Resulting fit parameters are indicated in the legend.

broadening mechanisms than free carriers are not accounted for.

If we insert Eq. (11) into Eq. (12), we get a direct relation between hole concentration and deconvoluted width

$$\Gamma_F = 2\eta^{5/3} (B \cdot c_h + p_0)^{2/3} + \Gamma_L. \quad (13)$$

In Fig. 5, the deconvoluted width Γ_F is plotted in dependence of the hole concentration together with the curve calculated by Eq. (13).

In addition to the described fitting of a convoluted distribution Gauss*Fano, we tested the direct fitting of a Fano curve to the data. The tests revealed that only the obtained width values differed significantly from the former results, whereas the Fano parameter remained nearly the same. In Fig. 5, the respective (non-deconvoluted) width Γ is shown. An empirical linear fit is applied, which is also used as a calibration curve for the mappings as described below.

FIG. 5. Raman peak width in dependence of hole concentration (by ECV). Triangles are as received widths Γ , on which an empirical linear fit is applied. Squares are the deconvoluted (i.e., reduced by the Gaussian width contributed by the measuring system itself) widths Γ_F , which is plotted together with a curve calculated by Eq. (13).

C. Injection depending Raman

As the Fano asymmetry to the Raman spectra is directly caused by the free carriers, which are inevitably generated during Raman excitation, the question of excitation intensity related effects is most obvious. In order to show that such an effect must be considered even for typical measurement conditions, we simulate the free carrier concentration during Raman excitation.

We assume a uniform illumination at 532 nm perpendicular to the front. The intensity corresponds to a light power of 3.3 or 33 mW within a spot area of $2\ \mu\text{m}$ in diameter. The reflection at an uncoated Si surface is subtracted. The fact that for typical Raman measurements, the illumination intensity is not uniform but focused is neglected. Therefore, exact agreement with experimental results cannot be expected.

The recombination is majorly due to Auger mechanism and recombination at the non-passivated front surface (assumed recombination velocity: $10^6\ \text{cm/s}$). For the sample, a boron doping concentration of $5 \times 10^{17}\ \text{cm}^{-3}$ is assumed. The calculation is made by means of the software PC1D.²¹

Fig. 6 shows the calculated profile of the free carrier concentration. At high excitation power, the hole concentration within the Raman depth is in the range of 2×10^{18} to $9 \times 10^{18}\ \text{cm}^{-3}$. Thus, the excited carriers are expected to significantly influence the Raman peak shape. Naturally both types of carriers are generated. However, as from experimental studies of p and n-type silicon, the effect of holes on the peak shape is expected to dominate.

Raman measurements of some of the mono-crystalline samples at various excitation powers in range of 2 to 40 mW were made. The output power of the laser was controlled prior to each measurement. As expected for intensity related effects, we found that the focusing of the laser onto the sample surface is critical for the results. We adjusted the focusing such as to obtain maximum intensity of the Raman peak.

As shown in Fig. 7(a), peak width and asymmetry increase with the applied illumination power. Even samples with the same doping and thus the same Raman parameters at low power may show different Raman parameters at high

FIG. 6. Simulated (PC1D) charge carrier concentration during Raman spectroscopy in the excited area. The minimum at the surface is due to recombination at the non-passivated surface. Particularly at high excitation power (i.e., 33 mW), the carrier concentration exceeds the indicated dopant concentration significantly.

FIG. 7. a) Deconvoluted width and Fano parameter obtained in dependence of Raman excitation power. Each symbol/line represents one sample with recipe no. indicated in the legend. (b) The deconvoluted width from (a) plotted versus the Fano parameter. The line is the dependence already obtained at 2 mW.

power illumination. This could be due to different surface characteristics (e.g., different surface recombination velocity).

In order to identify the mechanisms for peak deformation, the deconvoluted width is plotted against the asymmetry parameter (Fig. 7(b)), likewise the plot in Fig. 4 from which the linear curve is transferred. The plot shows essentially a similar dependence of the width as measurements at a constant power of 2 mW. A quantitative comparison to the fit obtained at low excitation power shows a small systematic deviation particularly at high powers. Heating of the probed sample by the exciting laser or the generation of n-carriers could be a reason for that.

D. Raman mappings

As a practical example for dopant mapping, we applied the calibration of Raman parameters to our silicon thin-film layers. Polished cross sections of the layers were mapped. In order to get acceptable measurement times, the integration time (per measured point) was much lower than before. Therefore, the signal to noise ratio of the spectra is much lower than before (cf. Fig. 1). An excitation power of 5 mW was chosen as a compromise.

As shown before, dopant concentration can be determined either by evaluation of the asymmetry parameter (calibration in Fig. 3) or alternatively by evaluation of the width (calibration in Fig. 5). Both methods are compared in

FIG. 8. Mapping of dopant concentration and stress by μ -Raman (at 5 mW) from a cross section of silicon layers. (a) Dopant concentration by evaluation of the Fano parameter. (b) Dopant concentration by evaluation of the width. Width evaluation results in much lower random scattering, so more details are revealed. (c) Peak position reveals high stress at the Si/SiC interface (bright boundary), which also contributes to the width. Corresponding values by width evaluation are therefore too high.

Figs. 8(a) and 8(b). They show similar results as for the high-low doping junction (Epi2/Epi1).

However, the asymmetry evaluation results in a significantly higher random error (about a factor of 4, i.e., $\pm 0.86 \times 10^{18}$ versus $\pm 3.3 \times 10^{18} \text{ cm}^{-3}$). Therefore, details of the doping distribution are much better revealed. As such, the small valley of the doping concentration at the seed/epi1 interface is clearly resolved in the width evaluation (Fig. 7(b)), whereas in the asymmetry evaluation (Fig. 7(a)), this feature is obscured by the scattering.

Additionally to the dopant concentration, the intrinsic stress values are evaluated from the peak shift. As can be seen in Fig. 8(c), the stress is low within the sample except for an about $3 \mu\text{m}$ wide boundary region near to the Si/SiC interface (cf. results published in Ref. 15). Within this region, the width is also increased. This simulates an increased dopant concentration in the width based mapping. In the asymmetry based mapping, such an artefact is not observed.

Further mappings were made at higher excitation powers of 20 and 50 mW. The random scattering of the mapped parameters decreased. Qualitatively, the results are similar; however, a quantitative evaluation of the dopant distribution would result in too high values.

V. DISCUSSION

The free hole concentration results in increased width and asymmetry of Raman peaks. We found quantitative relationships between hole concentration, peak width, and peak asymmetry. This dependence is similar for both, holes generated by doping or holes by light excitation, though the latter additionally creates free electrons. The prevailing effect of holes as compared to electrons can be explained by the smaller coupling of the phonon to the conduction band. We can thus apply the model of decoupled valence-conduction bands both in thermal quasi-equilibrium as described by the quasi-Fermi levels of each band for Raman scattering at high injection level.

Our interpretation of deformed Raman peaks at high excitation is in contradiction to results from Ref. 7, who interpreted the broadening of Raman peaks at high excitation as being the result of local heating and the asymmetry as being the result of a superposition of Raman peaks due to different temperatures in and outside the spot centre. We tested this hypothesis qualitatively by a calculation of superimposed

Raman peaks as they were suggested in this reference. Actually, the obtained peak is asymmetric but the asymmetric deformation is opposite to the experimental ones. Therefore, we conclude that the prevailing effect is due to not local heating but the result of hole generation. This conclusion is in agreement with published results found at much higher illumination power densities.²² Quantitatively however, we found a small difference of the broadening/asymmetry relationship of excited versus dopant holes, which could be due to temperature effects or else due to the influence of free electrons.

Both, evaluation of asymmetry or the width can be used to measure the acceptor concentration at levels of about 10^{18} cm^{-3} or above. The Raman excitation power must be kept low to avoid systematic errors from hole injection. The small offset in the determined asymmetry/dopant relation, likewise the small remaining asymmetry in case of the undoped sample, could be due to this.

For dopant mappings, the high number of measured points, together with a low excitation power and acceptable total measurement times may result in a low signal-to-noise ratio of the spectra. In this case, width evaluation is less prone to produce large random errors of the dopant value than asymmetry evaluation. The reason is that the width is majorly determined near the centre of the peak, whereas the Fano parameter is determined at the wings, where the remnant signal is low. On the other hand, width evaluation can result in too high dopant values in highly stressed regions, as may be identified by the analysis of the peak shift. No such effect can be found for the asymmetry parameter.

VI. CONCLUSION

Mappings of the acceptor concentration of crystalline silicon thin-film silicon layers have been made by means of micro-Raman spectroscopy. For calibration purpose, mono-crystalline Si layers were used with the dopant concentration determined by electrochemical capacitance voltage. As found by measurements at different injection levels, the effect on Raman spectra is similar for both, dopant or light induced holes, despite the free electrons generated in the latter case. Thus, measurements at high Raman excitation power result in too high values of determined dopant concentration.

Apart from asymmetry evaluation of spectra, width evaluation is newly introduced and compared with the former. The width method results in lower random errors for the dopant values, particularly at low signal-to-noise ratio of the spectra, which is typical for high resolution mappings. On the other hand, high stress also results in increased width, whereas no such effect has been found for the asymmetry. Therefore, the width analysis is preferable for mappings of samples with low stress, whereas for single point measurements, the asymmetry analysis is more reliable.

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