Extended Summary:

Nanostructure and phase formation in annealed a-$Si_{1-x}C_x$:H thin films for advanced silicon solar cells

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Motivation

Crystalline Silicon (Si) based solar cells are dominating the photovoltaic market and the situation is likely to continue for the next decades. Microelectronic concepts and processes were transferred to high efficiency Si solar cells and as a consequence high efficiencies were achieved. However, the development of high efficiency Si solar cells stagnated in the last years. In microelectronics Si nanocrystals (NCs) have been a subject of research for more than 15 years. Periodically aligned Si NCs in a dielectric matrix are a promising material for the application as an upper cell of a Si based tandem solar cell to realize very high efficiency solar cells. Recent modelling showed that a high density of Si nanocrystals within a SiC matrix has the highest potential, compared to SiO_2 or Si_3N_4, as a Si quantum dot absorber material [1]. To fabricate a Si quantum dot material by Plasma enhanced Chemical Vapour Deposition (PECVD) two different methods can be used: On the one hand a single layer approach, where the size of Si NCs is only controlled by the annealing conditions or a multilayer approach as proposed by Zacharias aiming at the control of the Si NCs by a stoichiometric diffusion barrier [2]. The emphasis in this paper is placed on the single layer approach.

Experimental approach

We present Si NCs in a SiC host matrix prepared by a simplified single layer approach. For the single layer approach a single Si-rich SiC (SRSiC) thin film (a-$Si_{0.8}C_{0.2}$:H) is deposited on Cz-Silicon with the orientation (111). Single layers are prepared in a PECVD system from the company Roth&Rau using a high frequency source and a microwave source for plasma excitation. Silane (SiH_4), methane (CH_4) and argon (Ar) are used as precursor gases [3]. Variations in the chemical composition within the thin films were solely achieved by changing the SiH_4 to CH_4 ratio during deposition. After deposition, a subsequent thermal annealing step, e.g. rapid thermal processing (RTP), is performed. The annealed single layers are hydrogen (H) passivated in a Remote Plasma Hydrogen Passivation (RPHP) reactor for a lower defect density.

Results:

We successfully deposited and annealed SRSiC single layers. The as-deposited SRSiC thin films are amorphous and contain a large amount of H. This was detected by Fourier Transformed Infrared (FTIR) spectroscopy. In Figure 1 FTIR spectra from rapid thermal annealed SRSiC thin films are shown.

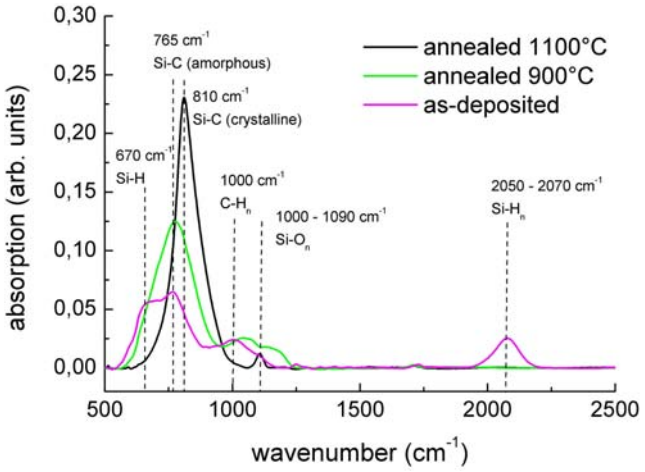

Figure 1: FTIR spectra of as-deposited and at various temperatures rapid thermal annealed SRSiC thin films.

After annealing at 900°C, all H related absorption modes are absent in the investigated films. The Si-C mode around 765 cm^{-1} changes its shape from a Gaussian to a Lorenzian distribution and the band shifts to higher wavenumbers. Responsible for the change in shape and the shift of the Si-C band is a restructuring from amorphous to crystalline SiC. The integrated area under the Si-C mode increases, due to the increase of Si-C bonds within the analyzed sample volume. During annealing, absorption modes around 1000 – 1090 cm^{-1} evolve, which are assigned to Si-O_n bonds, due to the a surface oxidation of the SRSiC thin films.
To control the size of Si NC, annealing at different temperatures is performed under Nitrogen (N_2) atmosphere either in a conventionally heated furnace or in a rapid thermal annealing furnace. Figure 2 (left side) shows X-ray diffraction patterns of SRSiC thin films annealed at different temperatures in the conventionally heated furnace.

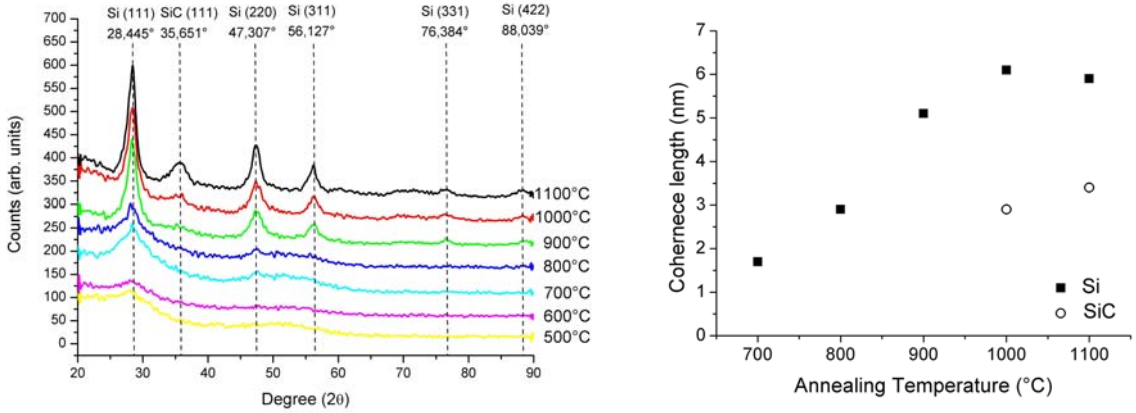

Figure 2: (left side) GIXRD measurement of SRSiC single layers annealed at different temperatures. (right side) Mean coherence length of Si and SiC NCs as a function of annealing temperature.

SRSiC thin films annealed up to temperatures of 600°C remain amorphous. No defined Bragg reflections are observable. A broad Bragg reflection at ~28.5° 2θ appears after annealing at 700°C and 800°C. This reflection corresponds to Si (111) lattice planes, thus Si NCs are formed within the SRSiC thin films. When annealing at higher temperatures than 900°C, additional Bragg reflections from Si (220), Si (311), Si (331) and Si (422) reflections become visible. At annealing temperatures exceeding 1000°C we observe the formation of SiC NCs, due to the occurrence of the SiC (111) reflection at ~35.6° 2θ, in addition to the Si NCs. The evolution of Si and SiC NCs with annealing temperature is shown in Figure 2 (right). The mean coherence length of the Si NCs was calculated using Scherrer's formula [4], which is an estimation of the mean NC size. After annealing at 700°C the mean Si NC coherence length is around ~2 nm and increases up to ~6 nm after annealing at 1100°C. The mean coherence length of SiC NCs increases from ~3 to ~3.5 nm, after annealing at 1000°C and 1100°C, respectively.

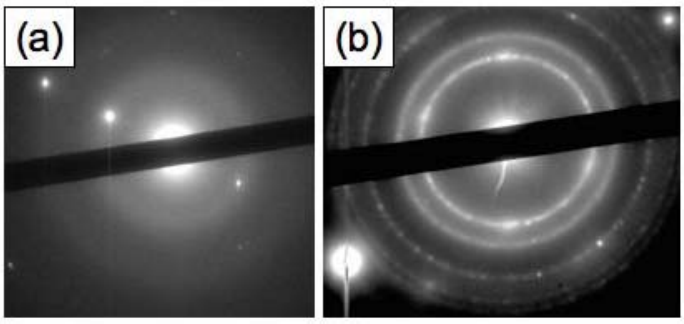

Figure 3: Energy filtered Ring Diffraction Patterns of (a) as-deposited SRSiC single layer and (b) annealed SRSiC single layer.

SRSiC single layers were investigated by TEM, therefore cross-section samples were prepared of SRSiC single layers annealed at 1100°C in a rapid thermal annealing furnace. In Figure 3 selected area ring diffraction patterns (SARDP) of an as-deposited single layer (a) and an annealed single layer (b) are shown. The as-deposited thin

film shows no defined diffraction rings, thus the film is amorphous. After annealing, defined diffraction rings are formed, which correlate with lattice spacings from Si and SiC NCs. This is illustrated in Table 1. The sharp reflections in the SARDPs originate from the Si substrate.

Table 1: Measured lattice spacings according to Figure 3 (b) compared with lattice spacings from Si and cubic SiC (3C-SiC).

Nr.	1/nm	d (nm)	Phase	d (nm)
1	6.34	0.315	Si (111)	0.314
2	7.81	0.256	SiC (111)	0.252
3	10.20	0.196	Si (022)	0.192
4	12.16	0.165	Si (311)	0.167
5	12.86	0.155	SiC (022)	0.154
6	15.19	0.132	Si (004)	0.136

In Figure 4 diffraction contrast TEM images are shown acquired in bright field and with different reflections in dark field mode. The dark-field images are particular useful and image Si and SiC NCs according to the reflection used for the acquisition. Figure 4 (a) is a bright field image in which NCs are observable in weak contrast. In Figure 4 (b) a dark-field image acquired with the Si (200) reflection is shown. The film appears dark and no defects at the interface were formed during annealing. In the dark-filed image (Figure 4 (c)), which is acquired with the Si (111) reflection only Si NCs with a (111) orientation are visible. Figure 4 (d) shows a dark-field image acquired with the SiC (111) reflection, where SiC NCs are visible. The density of (111) orientated Si NCs is considerably higher than the density of (111) orientated SiC NCs.

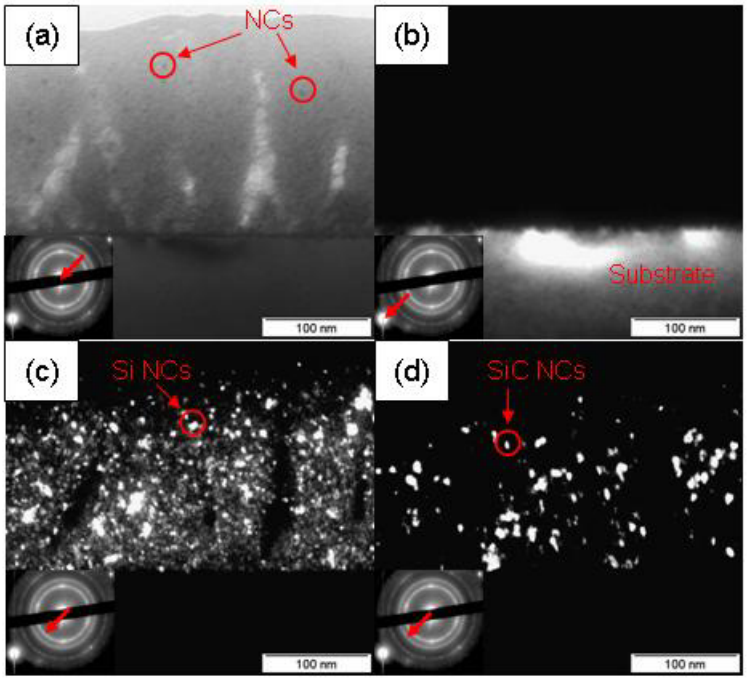

Figure 4: (a) Bright field image of SRSiC layer annealed at 1100°C. (b) Dark field image of SRSiC layer, acquired with the Si (200) reflection of the Si Substrate. (c) Dark-field image showing (111) oriented Si nanocrystals. The image was acquired with the Si (111) reflection. (d) Dark-field image acquired with SiC (111) reflection of (111) oriented SiC nanocrystals within the annealed SRSiC layer.

Directly after annealing photoluminescence (PL) spectra excited with an Ar-ion laser with a wavelength of 514 nm of the SRSiC single layers annealed at 700°C, 900°C and 1100°C, respectively, were acquired at room temperature. After annealing, the SRSiC thin films were H passivated to saturate dangling bonds within the dielectric matrix and at crystalline surfaces, which cause non radiative electron transitions. Before and after H passivation our SRSIC single layers are investigated by photoluminescence (PL) spectroscopy. Directly after annealing, the SRSiC thin film annealed at 1000°C and 1100°C show a broad PL signal with its maxima at 620 and 670 nm, respectively. SRSiC thin films annealed at lower temperatures show only a weak PL signal. The results are presented in Figure 5 (a). In Figure 5 (b) PL spectra of H passivated SRSIC thin films, previously

annealed at 700°C, 900°C and 1100°C, are shown. All H passivated SRSiC thin films show a broad PL signal around 1030 nm. The H passivated SRSiC thin film annealed at 1100°C shows additionally another broad PL signal around 670 nm.

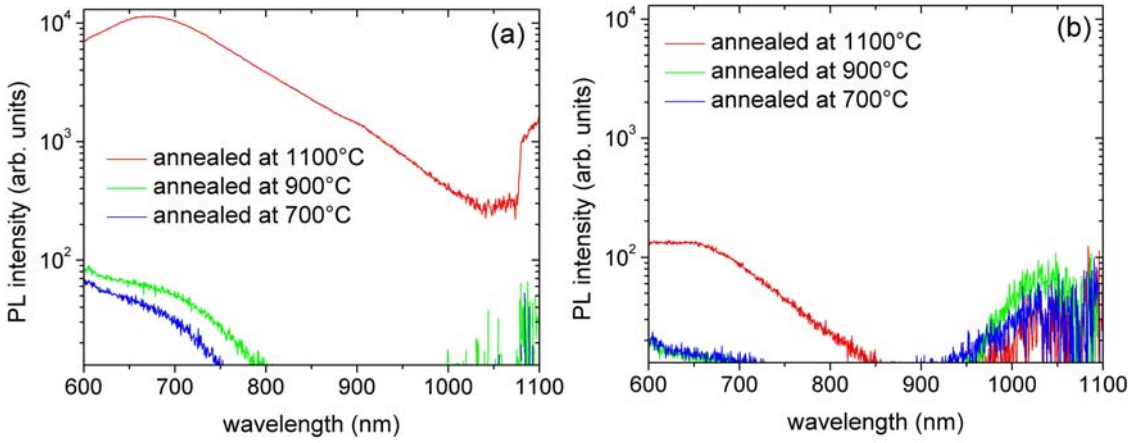

Figure 5: (a) Photoluminescence spectra of SRSiC single layers directly after annealing. (b) PL spectra of SRSiC single layers after annealing and H passivation.

Conclusion

We successfully fabricated Si NCs within a SiC matrix. During deposition a large amount of H is incorporated within the SRSiC thin films. After annealing H bonded to Si and C is absent. Crystallization of Si NC in SRSiC single layers starts at annealing temperatures as low as 700°C. As annealing temperatures exceed 1000°C Si NCs are accompanied by SiC NCs. In SRSiC thin film the density of SiC NC is lower than the density of Si NCs. The mean coherence length of Si NCs increases up to a temperature of 1000°C. After annealing at 1100°C, no further increase of the mean coherence length of Si NCs occurs. After defect passivation in a remote H plasma PL signals occurring in layers measured directly after annealing are quenched. After H passivation a PL signal around 1030 nm arises. This PL signal could be attributed to Si NCs with a large size dispersion [5, 6].

References

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