

## THERMAL STABILITY OF PECVD a-Si<sub>1-x</sub>C<sub>x</sub> LAYERS FOR CRYSTALLINE SILICON SOLAR CELL PASSIVATION

Stefanie Riegel<sup>1</sup>, Bernd Raabe<sup>1</sup>, Michael P. Stewart<sup>2</sup>, Hemant Mungekar<sup>2</sup>, Peter Borden<sup>2</sup>, Barbara Terheiden<sup>1</sup>, Giso Hahn<sup>1</sup>

<sup>1</sup> University of Konstanz, Department of Physics, Jacob-Burckhardt-Str. 29, 78457 Konstanz, Germany

<sup>2</sup> Applied Materials, 3050 Bowers Avenue, Santa Clara, CA 95054-3299, USA

Email: Stefanie.Riegel@uni-konstanz.de, Phone: +49 7531 88 2074, Fax: +49 7531 88 3895

**ABSTRACT:** We investigate the thermal stability of the surface passivation of PECVD a-Si<sub>1-x</sub>C<sub>x</sub> layers on symmetrical lifetime samples. To study the influence of thermal treatment on the passivation quality, lifetime measurements on symmetrical samples using the quasi transient technique and the quasi steady state technique are performed. The samples are exposed to temperatures up to 600°C. The annealing steps of ten minutes are carried out in H-plasma and N<sub>2</sub> ambient and annealing is done cumulatively. After each temperature step effective lifetime and FTIR measurements are performed. Maximum effective lifetimes of 1.2 ms and 1.7 ms are obtained after annealing at 550°C in hydrogen atmosphere generated by a remote H-plasma and N<sub>2</sub> ambient, respectively. In the FTIR spectra a reduction of the SiH peak intensity at 2060 cm<sup>-1</sup> is observed. The intensity of the other SiH peaks does not change significantly during annealing.

Keywords: silicon carbide, passivation, thermal annealing

### 1 INTRODUCTION

Amorphous silicon carbide (a-Si<sub>1-x</sub>C<sub>x</sub>) is an attractive passivation film for several solar cell designs. a-Si<sub>1-x</sub>C<sub>x</sub> layers provide an excellent passivation of both p- and n-type crystalline silicon surfaces with surface recombination velocities of less than 5 cm/s (p-type) and 54 cm/s (n-type) [1-3]. In previous experiments [4] a significant drop in passivation quality of the a-Si<sub>1-x</sub>C<sub>x</sub> layer after firing at a standard peak temperature for front side screen printing (800°C, 2 s) in a belt furnace was found. Effective lifetimes were reduced by 0.5-2 orders of magnitude down to 140 μs. In this paper we investigate the temperature stability of a-Si<sub>1-x</sub>C<sub>x</sub> in the temperature range from 80°C to 600°C in remote H-plasma (abbreviated H-Plasma in this work) or N<sub>2</sub> ambient (10 min at each temperature). This temperature range is very interesting for solar cell concepts based on LFC (Laser Fired Contact) annealing or Ni sintering steps. These steps are normally carried out at temperatures between 300 and 450°C.

The influence of deposition conditions and temperature treatment on passivation quality and bond densities of silicon carbide layers are investigated.

We perform a detailed study of the temperature stability of the passivation quality of silicon carbide layers and the influence of hydrogenation for the a-Si<sub>1-x</sub>C<sub>x</sub>/Si interface. a-Si<sub>1-x</sub>C<sub>x</sub> layers are deposited on n-type FZ wafers (1.5 Ωcm, 12 Ωcm). Depositions are carried out at Applied Materials using plasma enhanced chemical vapour deposition (PECVD) with different methane to silane ratios. Effective lifetimes are measured directly after deposition and after temperature treatment with H-plasma or N<sub>2</sub> ambient.

To determine the bond densities within the layers fourier transform infrared spectroscopy (FTIR) measurements of the samples are carried out before and after temperature treatment.

### 2 EXPERIMENTAL DETAILS

For sample preparation n-type FZ wafers of 1.5 Ωcm and 12 Ωcm base resistivity are used (thickness: 1.5 Ωcm: 525 μm, 12 Ωcm: 775 μm). As surface treatment before deposition heavily influences the passivation quality [5] wafers are cleaned in an H<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>SO<sub>4</sub> mixture at University of Konstanz (UKN) and receive a HF dip shortly before deposition at Applied Materials. a-Si<sub>1-x</sub>C<sub>x</sub> layers are deposited on both sides of the wafers using an AKT 4300 PECVD system. Depositions are carried out with four different methane to silane ratios (CH<sub>4</sub>/SiH<sub>4</sub>=A...D; A: low ratio, D: high ratio). Deposition temperature is 400°C in all cases.

Samples are exposed to temperatures ranging from 80-600°C in H-plasma and N<sub>2</sub> ambient. Samples are annealed for 10 minutes at each temperature, characterized (see below) and then the next temperature step is performed, i.e. temperature annealing is done cumulative.

Effective lifetimes are measured directly after deposition and after each temperature step using a WCT-120 Sinton lifetime tester. The 12 Ωcm samples are measured using the quasi transient technique, while the 1.5 Ωcm samples, due to their lower effective lifetime, are measured in the quasi steady state mode [6].

For the 12 Ωcm samples fourier transform infrared spectroscopy (FTIR) measurements are carried out after each temperature step. FTIR data is recorded from 400 to 4000 cm<sup>-1</sup> using a Bruker Vertex 80 system.

### 3 EXPERIMENTAL RESULTS

#### 3.1 Passivation quality

In Figure 1 the effective lifetimes of the **12 Ωcm n-type** samples are displayed. The a-Si<sub>1-x</sub>C<sub>x</sub> layers were deposited with the lowest ratio CH<sub>4</sub>/SiH<sub>4</sub>=A. Directly after deposition the samples show an effective lifetime of about 800 μs. In the temperature range from 200 to 300°C the sample treated in H-plasma seems to show a slight decrease in effective lifetime down to 725 μs after annealing at 300°C. For higher annealing temperatures

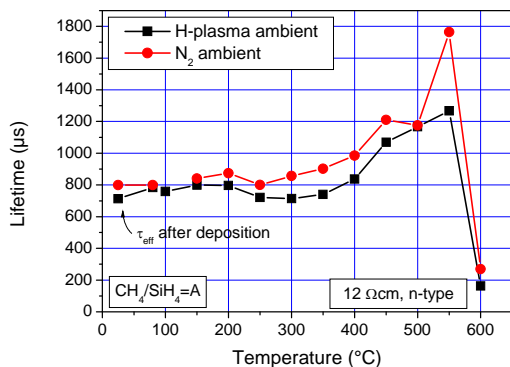
effective lifetimes improve to 1.27 ms at 550°C. The sample treated in N<sub>2</sub> ambient does not seem to respond to temperatures up to 300°C. Values for effective lifetimes fluctuate between 765 μs after annealing at 80°C and 875 μs after annealing at 200°C. For temperature treatment above 350°C effective lifetimes increase with increasing annealing temperature up to 1.76 ms after annealing at 550°C in N<sub>2</sub> ambient. This is an improvement in effective lifetime by a factor of 2.2 compared to the as deposited state.

After 10 min at 600°C effective sample lifetimes are reduced to 160 μs in H-plasma and 270 μs in N<sub>2</sub> ambient. Assuming infinite bulk lifetime these values correspond to SRVs of 240 cm/s (H-plasma) and 145 cm/s (N<sub>2</sub> ambient). Initial SRV directly after deposition is ~50 cm/s. The SRVs reached after temperature annealing at 550°C are 30 cm/s (H-plasma) and 25 cm/s (N<sub>2</sub> ambient).

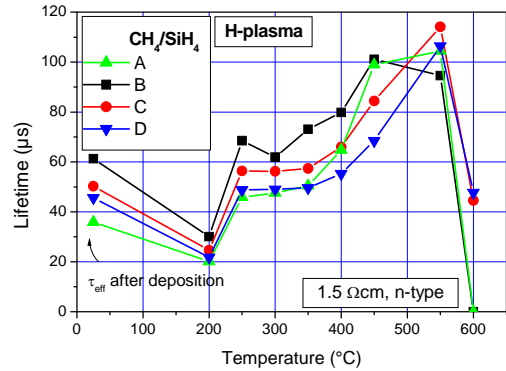
Effective lifetimes of the **1.5 Ωcm n-type wafers** are reduced to 30-60 μs due to processing problems. We assume that the cleaning of the surface (PIRANHA etch (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>, 3:1) followed by HF-dip (5%)) did not give optimum results.

As shown in Fig 2 and Fig 3, the effective lifetime of the 1.5 Ωcm sample drops down to 50% of the initial value for both ambients and for all values of CH<sub>4</sub>/SiH<sub>4</sub> after annealing at 200°C. If the samples are exposed to higher temperatures up to 550°C afterwards (the annealing steps are done cumulative) the effective lifetime recovers. The amount of recovery depends on the CH<sub>4</sub>/SiH<sub>4</sub> ratio and the annealing ambient.

Temperature treatment in H-plasma at temperatures of 250°C and above results in an increase in effective lifetimes. Layers deposited with the highest CH<sub>4</sub>/SiH<sub>4</sub>=D, C show an increase by a factor of 2.3 while layers deposited with medium CH<sub>4</sub>/SiH<sub>4</sub>=B show an increase by a factor of 1.5. The effective lifetime of the sample deposited with the lowest CH<sub>4</sub>/SiH<sub>4</sub>=A increases by a factor of 2.9. The lifetimes of the samples deposited with CH<sub>4</sub>/SiH<sub>4</sub>=A, C are too low to be measured with our WCT-120 tool after temperature annealing at 600°C. This means they are well below 5 μs.



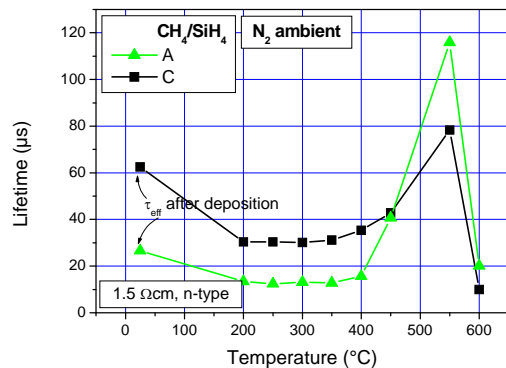
**Figure 1:** Lifetime measurements of the 12 Ωcm samples (CH<sub>4</sub>/SiH<sub>4</sub>=A) after stepwise temperature annealing in H-plasma and N<sub>2</sub> ambient. Samples are exposed to each temperature for 10 min. Maximum effective lifetimes of 1.27 ms and 1.76 ms are reached after temperature annealing at 550°C in H-plasma and N<sub>2</sub> ambient, respectively. The maximum effective lifetimes of 1.76 ms corresponds to a SRV of 25 cm/s (assuming infinite bulk lifetime).



**Figure 2:** Lifetime measurements of the 1.5 Ωcm samples after stepwise cumulated temperature annealing in H-plasma. Samples are exposed to each temperature for 10 min. CH<sub>4</sub>/SiH<sub>4</sub>=A means a low ratio, CH<sub>4</sub>/SiH<sub>4</sub>=D means a high ratio.

Figure 3 shows that in N<sub>2</sub> ambient the effective lifetimes remain at 50% of the initial value up to temperatures of 400°C. Temperature treatment between 450°C and 550°C leads to an improvement in effective lifetimes. Effective lifetime increases with increasing annealing temperature up to 4 times of the one measured directly after deposition.

One explanation for the significant drop after the first annealing temperature of 200°C for all 1.5 Ωcm samples could be the deterioration of the a-Si<sub>1-x</sub>C<sub>x</sub>/Si interface due to impurities. Defects created in this way may be passivated by hydrogen at higher annealing temperatures. The H-Plasma ambient can provide hydrogen for the passivation of interface defects, while the N<sub>2</sub> ambient does not provide additional hydrogen. Hence, the a-Si<sub>1-x</sub>C<sub>x</sub> layer must serve as a hydrogen source for the samples treated in N<sub>2</sub> ambient. Hydrogen bonded within the a-Si<sub>1-x</sub>C<sub>x</sub> layer must be released to be available for the interface passivation. Wieder et al. [7] observed, that hydrogen effuses from a-Si<sub>1-x</sub>C<sub>x</sub> layers at 350°C and above. Therefore, effective lifetimes of the samples treated in H-plasma increase at lower temperatures than for the samples treated in N<sub>2</sub> ambient.



**Figure 3:** Lifetime measurements of the 1.5 Ωcm samples after stepwise temperature annealing in N<sub>2</sub> ambient. Samples were exposed to each temperature for 10 min. The CH<sub>4</sub>/SiH<sub>4</sub> ratios are the same as in figure 2.

**Table I:** Vibrational frequencies of different functional groups [7-10]

Wavenumber [cm <sup>-1</sup> ]	600-650	760-770	900, 860	970	950-1110	1250	1340
Group	Si-H	C-H	Si-H	Si-O-Si	C-H	C-H	C-H
<b>1400</b>	<b>2000</b>	<b>2080</b>	<b>2880</b>	<b>2950</b>			
C-H	Si-H	Si-H <sub>n</sub>	C-H	C-H			

**Table II:** Vibrational frequencies detected in the samples examined in this work.

Wavenumber [cm <sup>-1</sup> ]	615	745	900	970	1110	1310	2060
Group	Si-H	C-H	Si-H	Si-O-Si	C-H	C-H	Si-H <sub>n</sub>

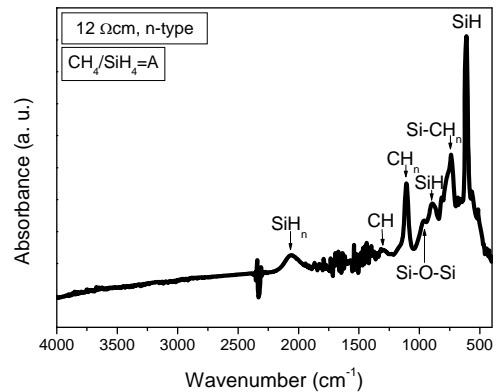
### 3.2 Bond densities

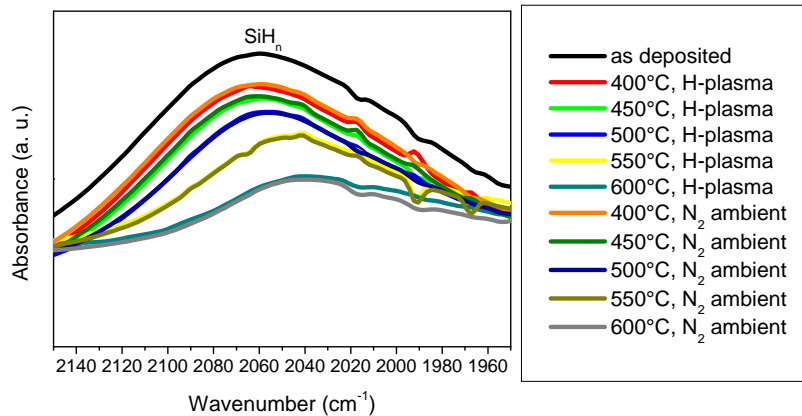
To determine the bonds in the a-Si<sub>1-x</sub>C<sub>x</sub> layers and at the a-Si<sub>1-x</sub>C<sub>x</sub>/Si interface fourier transform infrared spectroscopy (FTIR) measurements are performed. Figure 4 shows the FTIR absorption spectra of one of the 12 Ωcm n-type samples directly after deposition. a-Si<sub>1-x</sub>C<sub>x</sub> layers of 140 nm thickness are deposited on both sides of the wafer using the lowest CH<sub>4</sub>/SiH<sub>4</sub>=A. Table I gives an overview of different vibrational groups usually detected in a-Si<sub>1-x</sub>C<sub>x</sub> layers [7-10]. Seven of the expected characteristic absorbance frequencies are detected in the FTIR spectra of our a-Si<sub>1-x</sub>C<sub>x</sub> layers (see Table II). The detected peaks are the Si-H<sub>n</sub> related peaks at 615, 900 and 2060 cm<sup>-1</sup>, the C-H related peaks at 745, 1110 and 1310 cm<sup>-1</sup>, and the Si-O-Si related peak at 970 cm<sup>-1</sup>. The C-H<sub>3</sub> related peaks at 2880 and 2950 cm<sup>-1</sup> are not detected [8]. We trace this back to the low carbon flux. The Si-H related peaks at 2060 and 600-650 cm<sup>-1</sup> are commonly related to the stretching and wagging or rocking modes of SiH<sub>2</sub> and the peak at 900 cm<sup>-1</sup> to the bending mode of the polysilane chain (SiH<sub>2</sub>)<sub>n</sub> [9, 11, 12]. The CH<sub>n</sub> related peak at 745 cm<sup>-1</sup> owns a big shoulder in the long wavenumber regime up to 800 cm<sup>-1</sup>. Laidani et al. [10] related this peak to Si-C, while Lin et al. [8] assigned it to C-H<sub>2</sub> (770 cm<sup>-1</sup>) and Si-CH<sub>3</sub> and C-H (760 cm<sup>-1</sup>). Wieder et al. also related it to Si-CH<sub>3</sub> (780 cm<sup>-1</sup>) [7]. As the full width at half maximum of the peaks detected in this work is in the range of 10 cm<sup>-1</sup> to 90 cm<sup>-1</sup> we assume an overlap of these absorption peaks.

The only peak we observe in our work showing temperature dependence is the Si-H related peak at 2060 cm<sup>-1</sup> (see Figure 5). For an increasing temperature absorbance decreases and the peak shifts to smaller wavenumbers ending up at 2040 cm<sup>-1</sup> after annealing at 600°C. The reduction and shift of the peak do not differ for the sample treated in H-Plasma and the one treated in N<sub>2</sub> ambient. W.-L. Lin et al. suggested that this behavior is rather due to Si-H monohydride in a clustered environment than to SiH<sub>2</sub> dihydride [8]. With this assignment the shift of this peak during temperature annealing can be explained with an effusion of hydrogen atoms from the SiH<sub>2</sub> bonds during annealing [8]. In this way SiH monohydride is formed from SiH<sub>2</sub> dihydride. The characteristic peak of SiH monohydride is rather found at 2050 than at 2000 cm<sup>-1</sup> suggesting that most of the dihydride is located in a clustered form [8]. The fact

that Lin et al. observed this peak at higher wavenumbers (at 2080 cm<sup>-1</sup> before and at 2060 cm<sup>-1</sup> after temperature treatment) than we do is explained theoretically by Lucovsky [12]. He calculated that the frequency of this vibration is shifted from 2095 to 2056 cm<sup>-1</sup>, if for a second neighbor environment two silicon atoms and one carbon are assumed instead of one silicon and two carbons. This is consistent with the assumption made above, that the carbon content in our a-Si<sub>1-x</sub>C<sub>x</sub> layers is rather low. In the small wavenumber slope of the 2060 cm<sup>-1</sup> peak we observe dips and very weak peaks varying with annealing temperature and ambient at 2018, 1993 and 1968 cm<sup>-1</sup>. These dips and humps may be due to the Si-H monohydride related peak expected at 2000 cm<sup>-1</sup>,

With respect to the observation of Wieder et al. that multiple-bonded hydrogen leaves a-Si<sub>1-x</sub>C<sub>x</sub> layers at approximately 350°C while single-bonded effuses not until approximately 700°C, we expect a reduction of the peak intensities at 615 and 900 cm<sup>-1</sup> for annealing temperatures above 700°C [7]. For the same reason we relate the peaks at 615 and 900 cm<sup>-1</sup> not with SiH<sub>2</sub> but with SiH.

**Figure 4:** FTIR absorption spectra of a 12 Ωcm n-type sample after deposition. a-Si<sub>1-x</sub>C<sub>x</sub> layers of 140 nm thickness are deposited on both sides of the wafer (CH<sub>4</sub>/SiH<sub>4</sub>=A, lowest ratio).



**Figure 5:** FTIR measurements of two 12  $\Omega$ cm n-type samples after stepwise temperature annealing in H-plasma and  $N_2$  ambient, respectively. The sample is exposed to each temperature for 10 min. Going to higher annealing temperatures results in a reduction in absorbance at 2060  $cm^{-1}$  and a shift to smaller wavenumbers. This indicates a transition from  $SiH_3$  and  $SiH_2$  to  $SiH$  (see text).

#### 4 CONCLUSION

Our experiments show that a- $Si_{1-x}C_x$  layer passivation quality can be improved by a factor of 2.2 by thermal treatment after deposition at temperatures up to 550°C (data from 12  $\Omega$ cm n-type samples) resulting in a maximum effective lifetime of 1.76 ms and a maximum SRV of 25  $\mu s$ , respectively. This increase in effective lifetimes comes along with a decrease in peak intensity of the Si-H related peak at 2060  $cm^{-1}$ . As the improvement in effective lifetime in  $N_2$  ambient is as high as in H-plasma, we conclude that the hydrogen from the H-plasma does not diffuse into the a- $Si_{1-x}C_x$  layers or is not embedded into the bonding network of the layers. This assumption is supported by the fact that the Si-H related peak at 2060  $cm^{-1}$  shows the same behaviour for H-plasma and  $N_2$  ambient. As we do not observe temperature dependence in the absorption intensity for another peak, we think, that the increase in effective lifetime is due to a rearrangement of the SiH bonds within the a- $Si_{1-x}C_x$  layer. As a result of this reorganization the number of SiH bonds at the Si / a- $Si_{1-x}C_x$  interface increases while their number in the a- $Si_{1-x}C_x$  layer is reduced.

We assume that the reduction in effective lifetimes of the 1.5  $\Omega$ cm samples is caused by process related defects at the Si / a- $Si_{1-x}C_x$  interface. We explain the larger improvement in effective lifetimes under treatment in H-plasma with additional hydrogen available for the passivation of these defects.

The samples deposited with different  $CH_4/SiH_4$  ratios show similar behaviour after thermal post-deposition anneal. But as the effective lifetimes are very low it may be that the influence of the deposition conditions is not visible.

The fact that a- $Si_{1-x}C_x$  layers tolerate temperature treatment up to 550°C in H-plasma and  $N_2$  ambient allows for its application in novel cell concepts using laser fired contacts annealing or Ni sintering steps.

#### 5 ACKNOWLEDGEMENTS

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