Carbon in Multicrystalline Ribbon –Silicon for Solar Cell Application

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ABSTRACT: Carbon is one of the main impurities in multicrystalline silicon used for photovoltaic applications. Among other impurities, particularly EFG –ribbon-material is highly supersaturated with carbon with concentrations up to $10^{18}cm^{-3}$. Furthermore, mechanical stresses are found in wafer regions containing a high density of twin lamellae. By a combination of TEM, HREM, EDX and image simulation, this paper demonstrates that the high stress can be correla ted to the accumulation of carbon in the twin boundaries. The experimental results will also be compared with ab -initio structure simulations of the energy relaxation due to incorporated carbon.

1. INTRODUCTION

Multicrystalline silicon (mc -Si) is a low -cost material for photovoltaic applications. Wafers of mc-Si are produced by different techniques such as ingot casting, Tri -crystal growth or ribbon growth. The edge-defined film-fed growth (EFG) belongs to the latter method and is attractive since it allows the wafer production of high quality with a large output and low costs (Schmidt et al. 2002). Nevertheless, mc -Si generally contains impurities and crystal defects, such as grain boundaries and dislocations with a higher concentration than found in single -crystalline Si (Riedel et al. 2002). These microscopic defects influence the electrical and the mechanical properties of the wafers.

Macroscopically, EFG wafers are characterized by high local mechanical stresses, which are up to five times higher than in other mc-Si materials (Möller et al. 2002). It seems that this non -uniform, internal stress is not (or only partly) caused by dislocations. Corresponding investigations revealed that the highest stresses appeared in EFG-wafer regions of low dislocation density. Furthermore, TEM investigations demonstrated that in these strained regions a high density of twin lamellae occurred having line densities in the range of 10^{3}-$10^{4}cm^{-1}$. Microtwins, in general, cannot explain the formation of local stresses and, therefore, other sources have to be taken into consideration. Carbon is one of the main impurities in mc -Si. Particularly EFG wafers are highly supersaturated with carbon reaching concentrations up to $10^{18}cm^{-3}$. However, precipitation of SiC could not be detected by TEM so far. This might be related to the low oxygen concentration in EFG material. Oxygen precipitation promotes an agglomeration of SiC (Gösele et al. 1991).

The paper deals with the question if there is a correlation between local stress, microtwins and the high carbon concentration. One possibility concerns the incorporation of carbon in the twin boundaries instead of forming bulk SiC precipitates. By combining TEM techniques as well as structure and HREM image simulation the possibility was studied to detect such local carbon incorporation in microtwins.

2. EXPERIMENTAL PROCEDURE

As-grown EFG wafers with a size of 10x10 cm^2 and an average thickness of 300µm were used for topographical stress measurements. The local internal stress was determined by a birefringence

technique using a commercial system. Hereby the wafers were scanned with circular polarized infrared laser light. The resulting rotation of the polarization of the transmitted beam is related to the internal stresses inside the wafers (Gamarts et al. 1993). The lateral resolution of the system amounts to 200x200 μm^2.

Different TEM techniques were applied for structure characterization and chemical analysis. Conventional diffraction contrast investigations were performed on a Phillips CM20 T win microscope (acceleration voltage: 200 kV). High-resolution investigations (HREM) of twin boundaries were done on a JOEL JEM 4010 (400 kV). The chemical detection of carbon was tried to perform by EELS using a Phillips CM 20 FEG as EELS is capable to detect light elements. In the present case the method was not sensitive enough to reveal unambiguous results. Using the very thin samples (< 20 nm) for EELS measurements the carbon content was lower than the detection limit. For this reason an EDX system with a very sensitive detector at a CM20 FEG was used. The advantage of EDX is that thicker sample regions can be used, where the signal/noise ratio of the carbon signal could be improved. To avoid surface contamination by carbon, the samples were handled in a plasma cleaner for 30 s before inserting them in the microscope. Thereby it was possible to detect carbon in regions of the twin boundaries.

3. RESULTS AND DISCUSSION

Topographic stress measurements of the EFG-wafer revealed regions with high local internal stress correlating with a high density of twin lamellae (Fig. 1a and b). TEM investigations confirmed the presence of twin boundaries with a high density (Fig.1c). Other defects like precipitates were not found. Dislocations exist only in very low density in the twined regions. For EDX measurements the samples were <110> oriented with the {111}-twin boundaries parallel to the electron beam. Thereby, the most possible amount of carbon accumulated on the lattice plane could be collected. Line scans (beam ∅: 2 – 3 nm) were performed on numerous twin boundaries. An example is given in Fig. 2. The increase of carbon correlates with the position of the twin boundaries. Low deviations were caused by a small drift of the sample during the measuring time of several minutes. The increasing carbon concentration at the twin boundary is clearly visible although a quantisation is not possible. Comparing measurements on twin regions of multicrystalline silicon grown by ingot casting did not show any increase of the carbon concentration in the twin boundary.

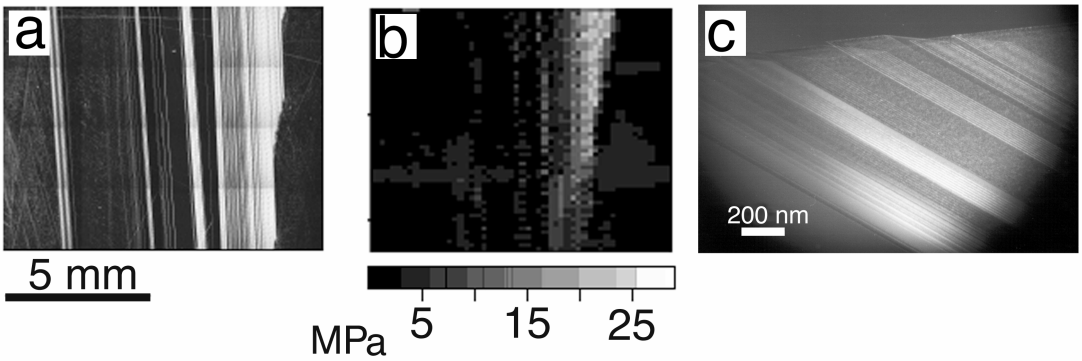

Fig. 1a,b: Optical micrographs of EFG material to determine the internal strain in microtwin regions. The structure (a) is correlated to stress measurements (b) of the same region. (c) Dark-field TEM micrograph of twin lamellas.

The presence of highly concentrated carbon in regions of the microtwin raises the question on its local distribution, i.e., if carbon is segregated as precipitates or substitutionally incorporated close or direct in the twin boundaries. By applying HREM and dark-field TEM we could not detect any agglomerates or precipitates in such regions. Therefore, we checked the possibility that the carbon atoms might be incorporated in the lattice of the twin boundaries. Different structure models have been analyzed. A possible substitutional incorporation of carbon in the twin plane is presented in

Fig.3. In this case it is assumed that the C atoms occupy a half of {111} double plane. Fig.3a shows the <110> projection of the crystal lattice of a regula r Si twin with distances of 2.35Å for all atoms, Fig.3b the same non -relaxed lattice with the C atoms. The relaxed twin structure with the corrected Si-Si bonds as well as Si-C bonds was received by applying ab -initio structure simulation to minimize the total energy (Fig.3c).

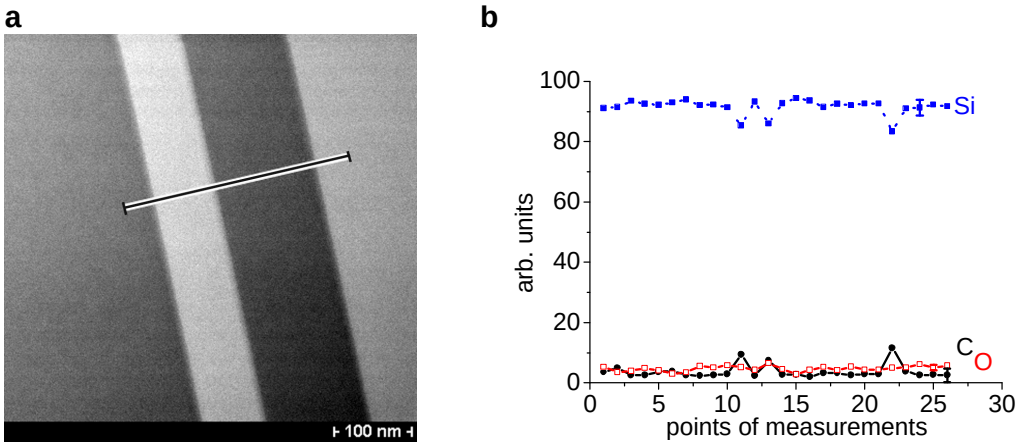

Fig. 2: (a) STEM micrograph of twin boundaries in <110> orientation. The EDX line scan of 270 nm length was performed with 26 measurement points. (b) The relative C concentration (lower curve) an d Si concentration (upper curve) measured by EDX along the line indicated in (a).

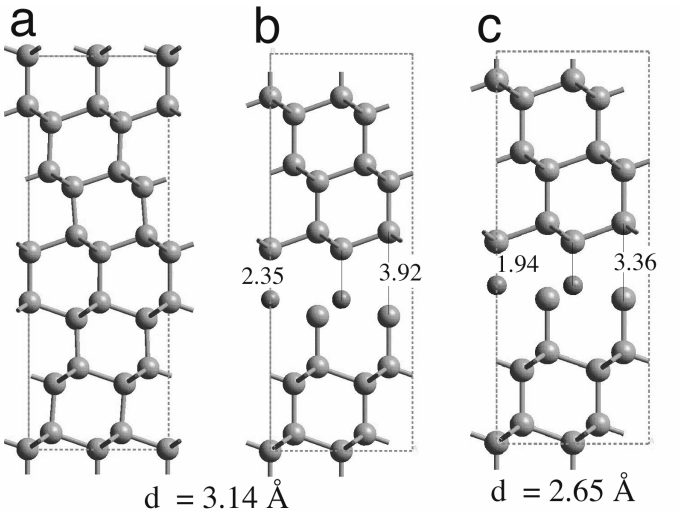

Fig. 3: Models using for the ab-initio structure simulation to minimize the total energy.
a) The start model of a Si twin structure with a {111} lattice plane distance of 3.14 Å
b) The same structure, but with a half of {111} double plane occupied with C atoms. In both structures the projected atom distances are given.
c) The energy minimized lattice. Due to the relaxation the lattice plane distance of the horizontal {111} plane is reduced by 0.5 Å.

Such a reduction of the {111} plane distance at a twin boundary should be detectable by HREM observation under appropriate imaging conditions. At first multi -slice calculations of twin structures have been carried out to analyze the influence of the imaging parameters, such as the defocus δf of the objective lens, specimen orientation and specimen thickness t. From such parameter set follows that C-induced {111} lattice plane shrinking should be visible near the Scherzer fo cus, where HREM images show the smallest delocalization effect at the interface. Furthermore, the deviation from the exact <110> crystal orientation is a critical parameter (Kaiser et al. 1999) and should be less than 1mrad. Fig. 4 presents a section of su ch numerous simulations using a twin structure as given in Fig.3c. The upper part shows the image for t= 20nm and δf=40nm assuming a 400kV -microscope with C_S=0.7mm (JEOL JEM 4010). The positions of the Si atoms on the {111} planes are superimposed; the C atoms in the twin plane are marked by white circles. As a characteristic feature, the twin boundary is characterize d by a non -symmetrical structure. The lower part of Fig.4 demonstrates the corresponding intensity plot of the {111} planes, which shows the “regular” lattice distance of the Si lattice outside the twin (as marked by 3x {111} planes on the right). The cent ral part

of the boundary is reduced by about 0.5Å, but this reduction does not correlate to a specific plane, but is expanded (marked by the black bar). Nevertheless, the reduction should be detectable in HREM images.

Numerous experimental HREM micrographs were taken from microtwin regions. It turned out that boundary regions are often strained and the lattice regions beside the boundary are slightly misoriented. The measurements of {111} lattice plane distances were only carried out at the best <110> orie nted boundaries. Fig. 5 presents an experimental HREM image of a twin boundary (marked by T). To measure changes of the perpendicular lying {111} planes templates of undisturbed Si lattice regions were inserted as shown by the box in the center. On the rig ht side, the fringes of twined lattice and the undisturbed matrix are aligned by their peaks of fringe intensities. On the left, a shift Δd of the {111} fringes of about 0.4Å±0.1Å is detectable. In our experimental HREM images only a reduction of {111} pla nes in the boundary regions could be observed. This shift is extended over 2-3 planes. It has to be mentioned that such a reduction of the lattice plane distance could not be observed in all EFG boundaries and samples of comparison.

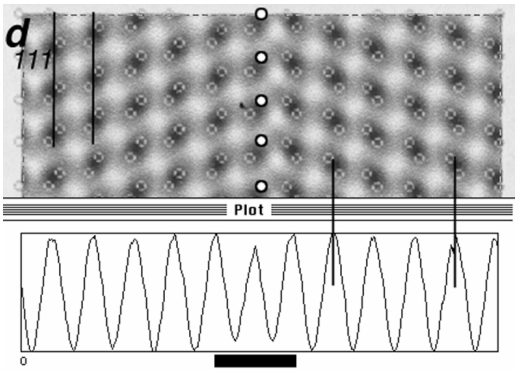

Fig.4: I mage simulation of a <110> oriented twin boundary containing a half of {111} double plane of incorporated C atoms (marked by circles). The lower part shows the corresponding plot profile of the {111} planes intensities. The peak positions mark the "mass ce nter". A slightly shrinked lattice in the center (Δd about 0.5Å) is marked by the black bar.

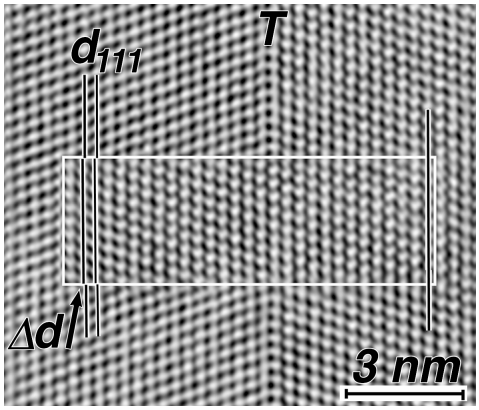

Fig.5: HREM micrograph of a <110> oriented twin boundary T. To demonstrate the reduction Δd of the {111} planes at the boundary, an image of a non -disturbed Si matrix is inserted (box in the center).

In conclusion, the present investigations give strong hints on the existence of substitutional C incorporation in twin boundaries in EFG material, which may be responsible for the high local stress in such wafers. The authors are aware of the limits of such an analysis and of the necessity to realize precise imaging conditions and a careful specimen preparation.

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REFERENCES

Gamarts E M, Dobromsyslov P A, Krylov V A, Prosenko S V, Jakushenko E A, Safarov V I, 1993 J. Phys. III France **3**, 1033

Gösele U, Tan T Y, 1991 in Material Science and Technology, Eds. R W Cahn, P Haasen, E J Kramer, (VCE: Weinheim) Vol **4**, 197

Kaiser U, Chuvilin A, and Richter W, 1999 Ultramicrosc. **76**, 21

Möller H J, Funke C, Lawerenz A, Riedel S, and Werner M, 2002 Solar Energy Mat. & Solar Cells.**72**, 403

Riedel S, Rinio M, Möller H J, 2002 Proc. 17th EPVSEC (ETA Florence) 1412

Schmidt W, Woesten B, Kalejs J P, 2002 Prog. Photovolt.: Res. Appl. **10**, 129