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3D-FIB investigation of Cu precipitates in c-Si after high temperature treatments

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Abstract

Besides x-ray fluorescence (XRF) and transition electron microscopy (TEM), 3-dimensional focused ion beam (3D-FIB) combined with scanning electron microscopy (SEM) is an additional method to investigate the transition metal distribution in crystalline silicon material leading to additional information on the 3D shape, size and distribution of precipitates. The 3D-FIB method has been used to investigate the transition metal precipitate distribution around extended crystal defects, showing a strong influence of crystallographic parameters on the precipitation behavior. In addition, the transition metal precipitate distribution after a phosphorous ($POCl_3$) diffusion process and a corresponding temperature profile alone has been investigated. During $POCl_3$ diffusion the transition metal precipitates dissolve and the transition metals move to regions with higher solubility leaving voids behind, which can still act as recombination active centers and have to be taken into account in further process treatments. The diffusivity and density of silicon self interstitials and the duration of the $POCl_3$ diffusion is not sufficient to fill the voids. If only the temperature profile of a $POCl_3$ diffusion is applied, the transition metal precipitates dissolve but return to the same sites during cool down due to a missing external getter sink.

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1. Introduction

Transition metals are among the most detrimental defects in multi-crystalline silicon material for solar cell applications, due to their impact on minority charge carrier lifetime. The content and distribution of transition metals

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is influenced by crystallization process parameters but also by solar cell processing steps, like gettering and high temperature treatments. To investigate transition metal precipitates in silicon, synchrotron based measurements like micro x-ray fluorescence (µXRF) [1, 2], or detailed TEM studies, e.g. [3], are usually necessary. It has been demonstrated that so-called 3D-FIB is also able to detect precipitates down to 5 nm in radius and provides additional information about the 3D shape, size and spatial distribution of the precipitates [4]. This 3D-FIB method has been applied to several samples before and after solar cell process treatments to investigate the influence of the respective processing step on the transition metal distribution.

2. Experiment

The investigated samples were intentionally contaminated by 20 ppma Cu in the melt during crystal growth to enhance the transition metal concentration in the Si material. Neutron activation analysis results in an overall concentration of approximately $1*10^{18}$ at/cm^3 Cu for the investigated samples. Falkenberg et al. [5] have demonstrated that electron beam induced current (EBIC) pre-characterization provides the possibility to prepare TEM lamellas exactly at the position of highly recombination active regions and therefore enhances the successful measurements of transition metal precipitates. The same approach can be used for 3D-FIB. A FIB cross-section has to be cut at the area of interest. Afterwards, single FIB cuts with a distance in the range of a few nm or tens of nm are performed. SEM images have been recorded automatically after each FIB cut and are further analyzed to extract only the transition metal precipitates within the investigated sample area. This analysis results in a 3D picture of the distribution of particles within the investigated area, which allows extracting additional information like the size and shape of the precipitates. Additional energy dispersive x-ray (EDX) measurements at larger particles in the µm-range allow to draw conclusions about the composition of these particles (exemplarily shown in [4]).

Beside detailed investigations of as-grown material, differently processed samples were also analyzed. The investigated process steps include a standard $POCl_3$ diffusion as well as a temperature treatment comparable to that of the $POCl_3$ diffusion but without P source.

3. Results

The detection limit of transition metal precipitates is influenced by the applied measurement parameters like SEM magnification and resolution, as well as the distance between two FIB cuts. For parameters used in this investigation, precipitates with r=8 nm can be detected, comparable or even better than for several µXRF facilities. Detection of even smaller precipitates has already been demonstrated by optimizing measurement parameters.

3.1. As-grown samples

As an example of local differences in the transition metal distribution at extended crystal defects, two different areas of interest on the same sample are shown: (1) a region around a Si_3N_4 inclusion, and (2) a highly recombination active defect in the centre of a grain. Both areas have been investigated in a control experiment by µXRF showing a high Cu concentration. In case of region (1) a remarkably high density of particles is detected. Up to 40 precipitates per µm² with an average radius of approximately 18 nm were found. For comparison, the corresponding µXRF measurements have shown only a diffuse Cu signal around the Si_3N_4 needle and not single precipitates [4].

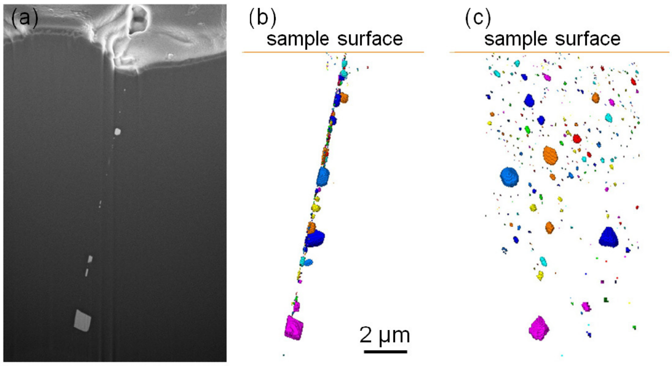

Fig. 1. (a) SEM image indicates different shapes of transition metal precipitates; (b) 3D reconstruction of the investigated sample area, view in the direction of FIB cuts. The Cu precipitates are perfectly aligned; (c) 3D reconstruction of (b) rotated by 90° to demonstrate the distribution of the Cu precipitates, their different sizes and shape.

The investigation of area (2) results in the detection of several larger precipitates assorted in a certain plane. Fig. 1 shows the 3D-FIB reconstruction of the precipitates from two different angles. Two different shapes are observed especially for larger precipitates: a disc-like shape and a more or less spherical or angular shape. The disc-like precipitates are located within the plane, while all precipitates with an angular shape stand out of the plane and just touch them from one side as can be seen in Fig. 1b. This leads to the assumption that local structural conditions of the Si matrix as well as stress fields strongly influence the formation of precipitates.

3.2. Influence of processing steps

After $POCl_3$ diffusion hardly any Cu precipitates are detected anymore. Instead several voids (up to 1 µm in diameter) are visible in the SEM images in Fig. 2. Additional EDX measurements show no Cu contamination at the voids or the surrounding area within the detection limits. Due to the high diffusivity of Cu in the temperature range of $POCl_3$ diffusions, the Cu precipitates dissolve and Cu atoms diffuse to the n-doped emitter region and the phosphorous silicate glass at the sample surface. Both regions show a higher solubility of transition metals compared to the p-doped Si base material and act therefore as a getter sink for transition metals. Diffusivity and density of Si self interstitials and the duration of the $POCl_3$ diffusion is not sufficient to fill the voids with Si. It has to be mentioned that these voids are still extended crystal defects which can act as recombination active defects as well as nucleation sites for other impurities and therefore affect the solar cell, even if the Cu concentration in the sample is decreased.

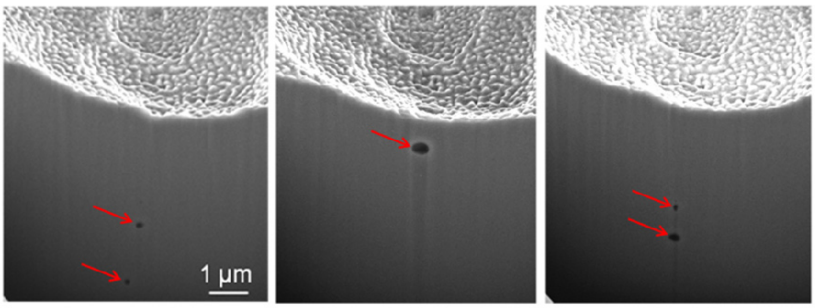

Fig. 2. Three single SEM images out of a 3D-FIB cross cut series: after P-gettering voids (indicated by red arrows) are detected and almost no Cu precipitates are found anymore.

If only the temperature profile of a phosphorous diffusion is applied to a sample, the 3D-FIB results are comparable to those of the as-grown sample. During the high temperature treatment Cu precipitates are dissolved and voids are left behind. Due to the lack of an external getter sink these voids act as nucleation sites for Cu precipitates during cool down resulting in a re-precipitation of Cu at the same sample area. This clearly demonstrates how careful temperature treatments during solar cell process steps have to be designed to avoid a re-precipitation of impurities at these voids.

4. Conclusions

3D-FIB closes the gap of missing 3D information of precipitate distribution, size, and shape compared to XRF and TEM studies. The advantages of 3D-FIB have been demonstrated in case of different areas of an as-grown sample which have shown similar µXRF results but a completely different distribution of Cu precipitates using 3D-FIB. The dissolution of Cu precipitates during $POCl_3$ diffusion and the beneficial gettering behaviour is well known. 3D-FIB allows a more detailed investigation of the defect structure of $POCl_3$ diffused samples resulting in the observation of voids after gettering which has to be taken into account in following process steps.

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