

Enhanced Phosphorus Diffusion at Microstructural Defects in Multicrystalline Silicon

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ABSTRACT

We have investigated the diffusion of phosphorus in multicrystalline silicon during solar cell emitter formation by secondary ion mass spectrometry (SIMS). From the experimental results, we observe significantly increased in-grain diffusion depths in areas of structural disorder that are not readily observed by the naked eye. It is believed that this effect is due to increased concentrations of silicon self-interstitials in the areas surrounding the defects, causing an enhanced transient response of elemental phosphorus diffusion.

1. Introduction

The use of multicrystalline silicon wafers as precursors for solar cells presently constitutes more than 50% of the overall industrial cell production, due to the relatively low cost of this material. However, the size, distribution, and crystal structure of the many crystallites contained in a wafer commonly differ considerably, causing spatial variations in material properties. Due to this, large differences in local defect density may arise. Of special importance during emitter diffusion, this may result in local variations in diffusion depths. Furthermore, even within what appears as a single crystallite, structural disorder is often present. Attributed to dislocation lines or coherent grain boundaries, e.g. due to twin formations, these crystal defects may act as areas of enhanced diffusivity during emitter formation.

The enhancement of phosphorus diffusion in silicon along grain boundaries is a well-known phenomenon [1]. Apart from at grain boundaries, however, diffusion profiles are regularly assumed uniform. In this work, we have studied the diffusion of phosphorus in multicrystalline silicon during the emitter formation step in solar cell processing. The results show that a significant increase in diffusion penetration can occur at areas of structural disorder within the grains of multicrystalline wafers that are not visible to the naked eye.

2. Experimental Details

Phosphorus diffused emitters were fabricated on p-type multicrystalline silicon wafers with resistivities in the range of 0.5-2Ωcm. The as-cut wafers were first exposed to a standard damage etch in order to remove any surface damage resulting from the wafer sawing. Then, to planarize the surfaces, a chemical polish consisting of HNO₃, HF, and CH₃COOH was utilized. The diffusion source Filmtronics

P509, consisting of a liquid glass containing phosphorus, was subsequently applied on the wafers by pressurized air spraying. Following an initial bake at 120°C to remove any solvents from the source, diffusion was carried out at 890°C at approximately 20 minutes in an IR lamp heated belt driven furnace, producing emitters with sheet resistances of about 40Ω/□. The residual diffusion glass was finally removed in dilute HF.

Following the emitter processing, secondary ion mass spectrometry (SIMS) was performed using Cs⁺ sputtering ions with a net energy of 13,5keV. The sputtered area was 200x200μm², whereas the analyzed secondary ions originated from an area with a diameter of 60μm centered in the crater.

3. Results and Discussion

Phosphorus diffusion profiles retrieved by SIMS from within the same crystallite are shown in Fig.1. Profile A1 was measured in a non-defected area of the crystallite, and was confirmed by repeated measurements within the crystallite. The profile is in good agreement with what is expected from modeling. For low temperature and high concentration phosphorus diffusions, the diffusion profile can be modeled as a dual process, i.e. a superposition of two different diffusion mechanisms with converging diffusivities at increasing temperatures [2]. For low-temperature diffusions, the characteristic kink as observed around 0.15μm in the profiles in Fig.1 represents the cross-over point at which the concentrations of the two regimes coincides.

Profile A2 in Fig.1 was retrieved from a different location within the same crystallite, separated from A1 by approximately 1mm. Interestingly, the analysis clearly shows a significantly increased phosphorus penetration for profile A2 in comparison to A1, the tail of the latter extending more than twice the depth into the wafer.

In order to gain knowledge on the origin of this enhanced diffusion, the sample was investigated by scanning electron microscopy (SEM) to reveal any differences in crystallographic quality of the areas in which the SIMS measurements were performed.

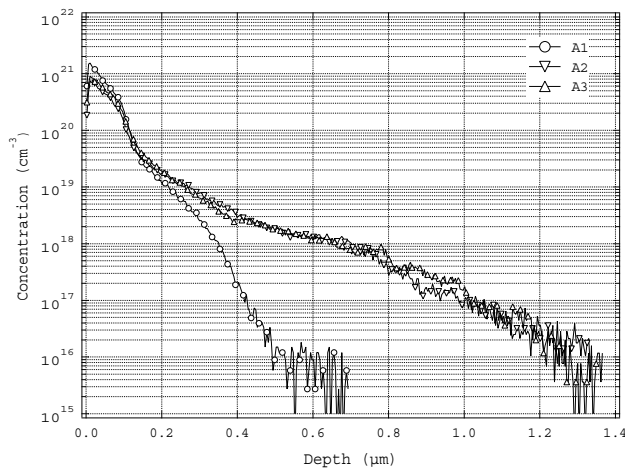


FIG.1 Phosphorus profiles retrieved by SIMS from different areas within the same crystallite.

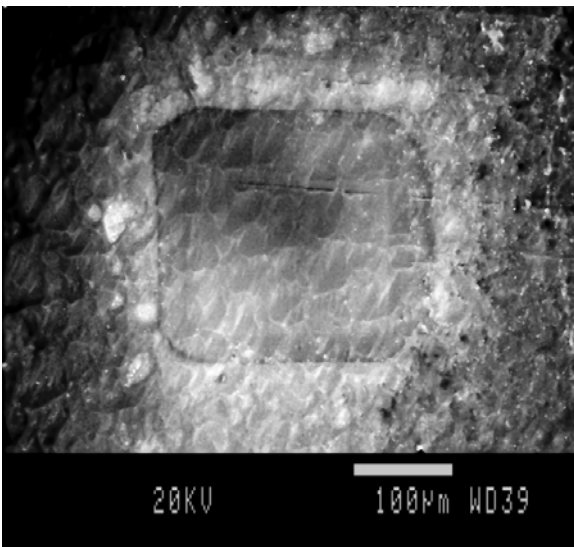


FIG.2. SEM image of the area in which diffusion profile A2 was measured.

Fig.2 shows a SEM image of the crater resulting from the SIMS measurement corresponding to profile A2. From the image, it is clearly seen that a defect line is present within the sputtered crater. Moreover, although not as easily distinguished in the image, it can be observed that the defect line extends well beyond the crater itself. This verifies that the defect is not resulting from the sputtering, but was indeed present at the time of diffusion. In conjunction with the diffusion profiles displayed in Fig.1, it thus seems that the presence of such microstructural defects, although small in extension, results in dramatically increased diffusion depths. Conversely, SEM investigations of the area in which profile A1 was measured did not reveal any such defects.

In order to ensure that the diffusion profile A2 was not broadened due to measurement errors, a third profile was measured approximately 3mm away from A2 along the extension of the defect line. The phosphorus concentration profile in this area is included in Fig.1, labeled A3. Clearly,

profile A3 follows A2 closely, providing validation of the correlation between the structural disorder and the increased diffusion depth.

It is well established that phosphorus diffuses in silicon primarily via interaction with silicon self-interstitials [3]. Hence, any variations in the density of point defects will influence the diffusion conditions significantly. For short diffusion times equilibrium point defect conditions may not apply, resulting in enhanced (or retarded) diffusivity. In the case of phosphorus diffusion in silicon, an enhanced transient response is frequently observed, attributed to a supersaturation of silicon self-interstitials [4,5]. In the areas adjacent to a microstructural defect, such as a dislocation line or twin boundary, a local increase in the concentration of self-interstitials is therefore a probable cause for the significantly deeper phosphorus penetration as observed in Fig.1.

Furthermore, from the profiles shown in Fig.1, it can be seen that only the tail part of the diffusion experiences an enhancement. The characteristic kink occurs at the same concentration and position, regardless of where the profile was measured. Thus, the high concentration part of the diffusion does not seem to be notably influenced by the locally increased density of self-interstitials, as opposed to the tail region as discussed above. In the diffusion model suggested by Hu et al. in [2], the slowly diffusing high concentration regime is assigned to phosphorus-vacancy pairs, while the tail region is ascribed to an interstitialcy-mediated mechanism. In conjunction with our results, we thus conclude that the locally enhanced penetration of the tail is due to injection of silicon self-interstitials around the microstructural defects.

4. Conclusions

We have shown that phosphorus diffusion along in-grain crystallographic defects can be significantly enhanced, resulting in an increased emitter penetration in these areas. This effect is attributed to a pile-up of dislocations and point-defect injection around the disordered area, causing a locally increased concentration of silicon self-interstitials promoting the phosphorus diffusion.

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