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Saw damage gettering for improved multicrystalline silicon

George F. Martins[a], Phi Macdonald[a], Toby Burton[a], Ruy S. Bonilla[a], Peter R. Wilshaw[a]

[a] *Oxford University, Department of Materials, Parks Road, Oxford OX1 3PH, UK*

Abstract

In this work we describe a technique, namely Saw Damage Gettering (SDG), which improves the lifetime of highly contaminated multi-crystal silicon wafers. The wafers to which it is applied are from the top and bottom of ingots, the so called “red zones” of ingots. Such wafers are currently discarded before processing due to high impurity levels which result in low efficiency cells. SDG entails an extra annealing step before the saw damage is removed by etching. The effect of the anneal is to dissolve metallic precipitates present in the material after casting. On subsequent cooling precipitates are preferentially nucleated in the high defect density regions associated with saw damage at the surfaces of the wafer so leaving the concentration of impurities in the bulk of the material significantly reduced. The anneal conditions, typically ~850 °C for ~20 minutes, are chosen so that the majority of metal precipitates dissolve. The cooling step, taking ~ 30 minutes, is such that the impurities have sufficient opportunity to diffuse from the center of the wafer to the damaged regions at the edges. This processing is found to improve carrier lifetimes by up to a factor of 4. This enhancement may be sufficient to enable red-zone wafers to be processed in the same manner as other, higher quality, mc-Si wafers without sacrificing cell efficiency. SDG is expected to be cost effective and easily incorporated into current cell processing procedures.

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1. Introduction

Currently over 85% of all solar cells produced are made out of silicon. The cost of producing single-crystal silicon, using the Czochralski method, remains the major limitation of this type of material. Multi-crystalline silicon (mc-Si), on the other hand, is produced using a much simpler and cheaper casting process. Solar cells produced from mc-Si ingots, however, perform worse than their single crystal counterparts, due partly to the moderate concentration of impurities remaining after the casting process. During casting, a large number of impurities present in the feedstock are dissolved in the melt. The bottom of the ingot, which solidifies first, has a high level of impurities as these diffuse in from the crucible during the remaining solidification process. The top of the ingot is

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also highly contaminated because impurities segregate into the melt during solidification so resulting in progressively higher impurity concentrations as solidification continues. The resulting ingots thus contain 15-20% of so called “red zone” material, that is the high impurity regions at the top and bottom of the ingot. In these regions the impurity concentration is sufficiently high that the material is no longer suitable for solar cell manufacture[1]. Gettering processes are used to produce a reduction in the concentration of contaminants in mc-Si. However, the standard methods are not sufficient to recover the quality of red zone material which is thus discarded. In this work we propose a simple gettering process, namely Saw Damage Gettering (SDG), which can reduce the impurity concentration in red zone mc-Si to a level at which the material may be re-introduced into conventional cell manufacturing lines.

In SDG, wire sawn mc-Si wafers are subjected to a thermal process in which the dislocations and cracks left at the wafer surface after sawing [2] provide nucleation sites for impurity precipitation. Gettering of impurities is competitive between all gettering sites. Therefore, maximizing gettering to a specific sink is enhanced by the removal of other competing sinks. In particular, precipitates initially present in mc-Si wafers are potent impurity sinks [3]. Many of these metal precipitates can be removed by annealing at sufficiently high temperatures for sufficiently long times. This moves the metallic impurities into solution where, on cooling, they become supersaturated. They will then tend to precipitate on any remaining precipitates, at dislocations, grain boundaries or other defect sites. The effectiveness of SDG lies in the fact that by far the highest concentration of potential precipitation sites is associated with the saw damage present at the wafer surfaces. This potentially enables the majority of the metal impurities, which were originally distributed throughout the wafer, to be locked into precipitates nucleated on the surface saw damage. A variable cooling rate is used to ensure that the impurities in solution in the bulk of the wafer have sufficient time, as cooling progresses, to diffuse to the saw damage regions. Longer times are required at the lower temperatures due to decreased diffusivity at these temperatures [4]. After SDG it is intended that the wafers are returned to the standard cell processing line where the next step is the conventional procedure to chemically remove the damaged surface regions (which now contain most of the metallic impurities).

2. Experimental methods

1-3Ωcm p-type mc-Si wafers, supplied by REC solar, were used for this work. Wafers were taken from the top and bottom red zones. In order to test the effectiveness of SDG pairs of specimens were produced in which one wafer still had the saw damage present whilst the other had had it removed. The pairs of specimens were taken from immediately adjacent “sister” wafers in the ingot and so had very similar defect distributions. In the following those wafers annealed with the saw damage present are considered to have undergone the SDG process, whereas those annealed after the saw damage had been removed are termed control specimens. Comparison between the two enables the efficiency of the surface damage regions at removing impurities from the bulk to be assessed. The full processing to which the wafers were subject is shown in figure 2. For each set of annealing conditions investigated, six pairs of sister wafers were used. The data from the SDG specimens and from the control specimens were each averaged to produce two data points, one for SDG and one for the control.

Saw damage was removed, see figure 2, after the SDG anneal (for SDG specimens) or before the anneal (for control specimens) by etching for one hour at 60°C in tetramethylammonium hydroxide (TMAH). All wafers were given an RCA clean, followed by an HF etch before the anneal step. The wafers were then loaded into a pre-cleaned quartz furnace tube and arranged into stacks with wafers separated from each other by cleaned quartz spacers at their corners. The tube was flushed with nitrogen for a period of 20 minutes prior to heating to limit oxidation during SDG. The tube was inserted into a furnace pre-heated to the set temperature, held a constant temperature for the anneal time and then cooled. The cool was arranged such that the cooling rate was slower at lower temperatures, see figure 1. In this way the characteristic length for impurity diffusion $L = (Dt)^{1/2}$ was the same for all temperature intervals. For this work D is taken to be the temperature dependent diffusivity of iron. The effect of this cooling profile is to maximise the opportunity for impurities to reach the surfaces of the wafer. Specimens were removed from the furnace when the temperature reached 500°C. In every experiment the rate of cooling at any particular temperature was kept the same and had a value that can be inferred from the graph in figure 1. The cooling process was approximately 30 minutes in duration being shorter at lower anneal temperatures.