SILICON RIBBONS BY THE STTRECH PROCESS: DIFFUSION LENGTHS OF SAMPLES WITH HIGH OXYGEN CONTENT

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ABSTRACT: We report the first measurements of diffusion length in high oxygen content silicon ribbons obtained by the STTRECH process.

The aim of this process is to produce thin ribbons of crystalline silicon with sufficient quality for solar cell fabrication. If the process is carried out in an oxydizing atmosphere, ribbons show very high oxygen content, as seen by infrared absorption. The diffusion lengths of some of these ribbons were measured, using the surface photovoltage and Schottky barrier short-circuit current spectral response techniques. We expected that the high oxygen content would lead to poor diffusion lengths. Surprisingly we found widely scattered values, with relatively high diffusion lengths in some of the samples, and a significant improvement of L_n with heat treatments typical of junction formation by diffusion (900 C for 1 hour). In fact in some 90 μm thick ribbons L_n reached values over 40 μm from a measured 10 μm in as-grown material. This raises the hope that this material might, after all, be considered a possible candidate for thin solar cell bases.

1. INTRODUCTION

We have been developing a technique of silicon ribbon production (STTRECH) which consists in the thickness reduction of a pre-ribbon during a zone melting recrystallization process [1]. The concentrated radiation from halogen lamps establishes a molten zone, across the whole width of the ribbon, which is scanned along its length. The relation between feed and pull velocities determines the final thickness of the ribbon.

Here we report the first measurements of minority carrier diffusion length in ribbons produced with this technique in a strongly oxidizing atmosphere. These samples show very high oxygen content, as seen by infrared spectroscopy. Although a little oxygen can improve the electrical behaviour of some ribbon material [2], in general a correlation is found between minority carrier lifetime reduction and increasing oxygen concentration [3]. These ribbons were not, therefore, being considered as possible substrates for solar cells, since such high oxygen concentrations should result in very poor diffusion lengths. Some measurements were made, however, using the surface photovoltage and the Schottky barrier short-circuit current spectral response techniques.

2. EXPERIMENTAL PROCEDURE

As test pre-ribbons for our process, we used rectangular slabs cut from policrystalline p-silicon wafers of Silso from Wacker and of ENE material. These slabs were then recrystallized with thickness reduction in our optical furnace. The final thickness ranged from 90 to 250 μm depending on the reduction ratio used in our process.

The samples thus obtained were characterized by infra red (IR) absorption spectroscopy, for measurement of oxygen content, and by surface photovoltage (SPV) and Schottky barrier short circuit current spectral response techniques, for the measurement of minority carrier diffusion length.

The Schottky structure consisted of a transparent titanium layer (10 nm) with Ag fingers and an aluminium back contact. The samples for SPV measurements were simply immersed in a solution 20% HF in water for a few minutes.

The samples without the Schottky barrier were characterized as grown, then submitted to heat treatments at a temperature of 900 C and characterized again.

A few samples were analysed for impurity content by glow discharge mass spectroscopy (GDMS).

3. RESULTS

When a silicon pre-ribbon is zone melted and recrystallized in an oxidizing atmosphere, we find that the resulting ribbon has an oxygen concentration equal to the solubility limit of this impurity in silicon.

The interstitial oxygen concentration (O_i) was determined by infra red absorption spectroscopy, corrected to include multiple reflection effects [4]. We used the IOC-88 (3.14E17 atoms/cm^2) calibration factor to convert absorption coefficient in the 9 µm band, obtained from spectra such as that shown in fig.1, to concentration values. The measured O_i was for all ribbons 1.7E18 atoms/cm^3.

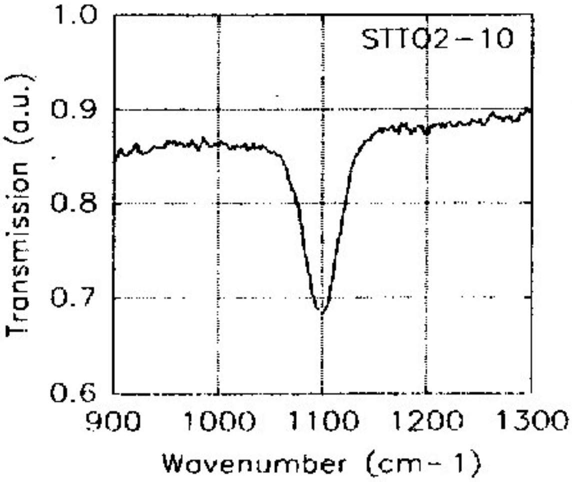

Fig.1- IR transmission spectrum showing absorption band due to interstitial oxygen.

Etching the samples in Wright etch revealed no precipitates when observed by optical microscopy.

The results obtained both by SPV and Spectral Response vary widely, from the expected very poor diffusion lengths to unexpected high values in some of the samples. In fact, while in some ribbons we measured diffusion lengths below 10 µm, in others L_n reached values over 40 µm.

One example of the results obtained for the spectral response of the short circuit current, in a 150 µm thick ribbon with a Schottky structure, is presented in fig. 2. The diffusion length in this sample (36 µm) is larger than the diffusion length obtained in a sample cut from the same wafer but processed in argon (20 µm) and that of the original wafer used as pre-ribbon (9 µm). Impurity analysis by glow discharge mass spectrometry (GDMS) in these samples revealed very high titanium concentration in the starting material, which is a known lifetime killer in silicon. Part of the increase in diffusion length in these samples should be the result of titanium concentration reduction (around 3 orders of magnitude) after the optical zone melting.

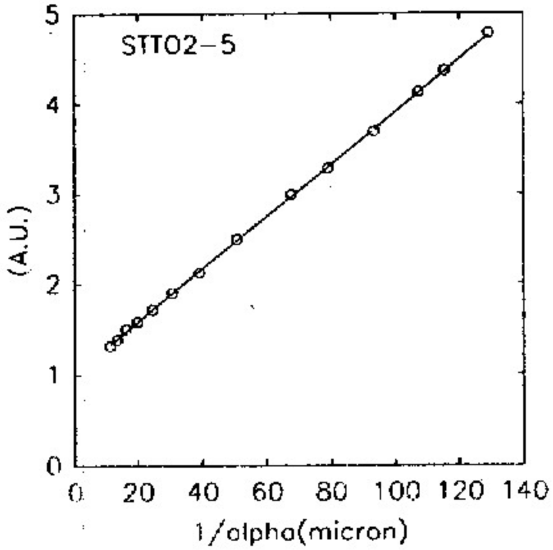

Fig. 2- Photon flux versus inverse absorption coefficient at constant short-circuit current in a device made on substrate STTO25 (as-grown) with very high oxygen content. Diffusion length L_n is 36 µm.

In fig.3 we present the results for sample EN15, obtained at constant surface photovoltage, showing a significant increase in the minority carrier diffusion length after a heat treatment at 900 C during 1 hour. The time and temperature chosen are typical for junction formation.

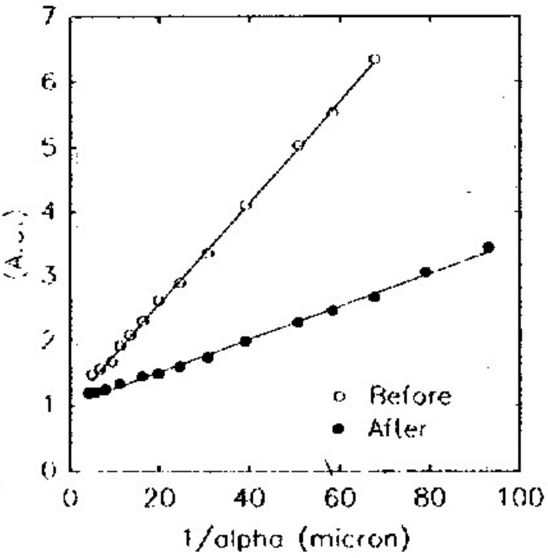

Fig. 3- Photon flux versus inverse absorption coefficient at constant surface photovoltage for substrate EN15, with the same oxygen content as that in fig. 1. Curves refer to data obtained in as-grown material and after 1 hour at 900 C. Diffusion length improved from 9.8 to 41 µm.

In a few samples, we investigated further the effect of thermal history. The results are displayed in Table 1. While the samples grown in argon atmosphere monotonically improve with further heat treatment, the diffusion length of the samples with high oxygen content seem to go through a maximum and then degrade with long exposures to 900 C. This fact may well be part of the explanation of the wide variation in diffusion lengths measured in as-grown ribbons with high oxygen content: since the thermal history of the ribbons was not the same, large variations are possible.

Table 1- Effect of heat treatment time at 900 C in minority carrier diffusion length (in μm).

Atmos-phere	Sample name	As grown	1 hour	+ 7 hours	+ 1/2 hour: junction formation
argon	AR100A	17.0	21.7	24.9	27.7
argon	AR100AB	9.5	10.0	20.2	30.0
oxidizing	1OR180	24.5	34.8	10.8	7.4
oxidizing	EN15	9.8	40.7	12.2	8.5

4. CONCLUSION

The reasons for the wide variation in behaviour of silicon ribbons with high oxygen content are not yet clear; however, the simple possibility of reasonable diffusion lengths has raised hopes that this material could be considered as a possible candidate for thin solar cell bases.

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