

AN APPROACH TO SOLARGRADE SILICON LAYERS
EPITAXIALLY GROWN ON MG SILICON SUBSTRATES

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Summary

We report about a study on the preparation of mg-Si substrates for growing silicon solar cells by CVD. Two processes for preparing mg-Si substrates are investigated: (1) The substrate is etched to a thickness which is in the range of the grown layer thickness. (2) Prior to deposition, a gettering process with a-Si is applied to the substrates. The applicability of a-Si gettering to silicon of varying purity has been demonstrated by results from I-V measurements and photoresponse measurements of pn-junctions prepared on these substrates.

1. INTRODUCTION

A comparison of results obtained from diffused and epitaxial solar cells made on different mg-Si substrates show significantly better results for epitaxial cells (1). In the latter case the requirements for the substrate to be met are the following: (A) good crystallinity (B) the number of impurities diffusing from the substrate into the epitaxial layer must be reduced to the SoG level (2). Especially metals which are present at high concentrations in the substrate are diffusing fast in the growing layer. We suggest two processes to meet the requirements stated in (B): (i) Use of very thin substrates (thickness in the same range like the one of the deposited layer). In this case the doping of the epitaxial layer by outdiffusion is limited by the total impurity content of the substrate rather than by the impurity concentration. (ii) Removal of a large amount of fast diffusing impurities. Taking into account the applicability to a large scale production, it is desirable to integrate the gettering process in the CVD process itself. Gettering by heavily damaged silicon surfaces is well known (3-5). The method suggested here is to deposit an a-Si layer on the substrate instead of inducing a damaged surface on the substrate. This is done in situ prior to deposition of the epitaxial layer.

2. EXPERIMENTAL

Substrates from single crystal silicon (CZ $\langle 100 \rangle$ oriented 6-10 cm p-type), polycrystalline silicon (SILSO Wacker Chemitronic, p-type), and mg-Si (pulled from the melt without significant purification) were used. Substrate size was either 1.5 x 1.5 cm² or 1 cm diameter. Chemical vapor deposition was carried out in a conventionally operated CVD system (rec-

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tangular reactor and RF-heated susceptor). pn-junctions were either formed by depositing n-type layers on the substrates using PH₃ as the dopant gas or by P diffusion from a P₂O₅ source. For gettering with a-Si the same CVD system was used. In the case of epitaxial layers, the gettering was carried out either in situ prior to deposition or after the layers were grown. If P diffusion was made the substrate was gettered before the diffusion. Additional doping of single crystals with Au was carried out by evaporating Au onto the substrate surface and subsequent solid state diffusion.

pn-junctions on gettered and ungettered substrates were examined by I-V measurements in the dark and under illumination as well as by spectral response measurements. The minority carrier diffusion length in the base region was obtained with a short circuit current method using published values for the absorption coefficient (6,7).

On mg-Si substrates etched to thicknesses ranging from 30-100µm n-Si, layers, 7-50µm thick, were grown. For van der Pauw measurements of the epitaxial layers, the substrates were removed by wet etching.

3. RESULTS AND DISCUSSION

3.1. a-Si gettering of mg-Si substrates

Considerations with simple assumptions (not taking into account grain boundary effects or high impurity concentrations) are made. As a result a-Si gettering should be effective on fast diffusing impurities since the gettering rate G_I should be proportional to $D_I \times t_a$ where D_I is the diffusion coefficient in the crystal and t_a the annealing time. For Cu and Ni experimentally determined values of G_I for ion damaged silicon gettering are published (3). For Ti G_I was calculated from the following equation (3):

$$G_I = C_I D_I t_a / d \quad (3.1)$$

where C_I is the solid solubility in the crystal, d is the substrate thickness and the other expressions are the same as above. Although the use of C_I in the equation does not seem to be a good assumption when applying a-Si the calculated G_I could give a rough idea of the gettering effect to be expected. Table I shows calculated values of the impurity concentration N_I in the layers grown on mg-Si substrates taking into account (i) the effect of a thin substrate (ii) gettering with a-Si using gettering rates described above. The values are evaluated from the diffusion equation for typical growth conditions. In Table II measured values of the Hall mobility μ_H and the resistivity ρ of epitaxial layers on gettered substrates are compared to μ_H and ρ obtained for mg-Si substrates. ρ of the layers corresponds to the dopant concentration expected from the results on pure substrates. μ_H is very close to values of μ_H in pure single crystals with the same dopant concentration (7).

3.2. Gettering of Au by a-Si in single crystal substrates

The effect of a-Si gettering is demonstrated on Au doped substrates. Au is one of the best known fast diffusing interstitial impurities in silicon. Pure single crystal substrates are used in order to exclude any additional effect from grain boundaries or other impurities. The solid state diffusion was made under conditions where the effect of substitutional doping is negligible (7). a-Si was deposited on two samples of a series of three. One sample with a-Si and one without a-Si were annealed for

30 min. The second sample with a-Si was annealed for 60 min at the same temperature. After the a-Si was removed by wet etching, P was diffused simultaneously in the three samples. Results of the measurements of the minority carrier diffusion length are shown in Fig.1. Fig.2 shows the influence of the remaining Au on the reverse biased diode in the dark.

3.3. Effect of a-Si gettering on solar cell parameters

The influence of gettering on the solar cell performance is demonstrated with pn-junctions on polycrystalline SILSO material with different cell configurations. Two junctions were prepared simultaneously for each experiment. One junction was gettered with a-Si. AM1 efficiencies of the un-gettered control cells and the gettered cells are compared in Table III. Fig.3 shows the photoresponse $s(\lambda)$ for the gettered cells relative to $s(\lambda)$ of the control cells. From the improved values in the short wavelength range for gettered cells, the effect of the gettering process as a function of the distance from the surface can be clearly seen.

4. CONCLUSIONS

The applicability of a-Si gettering of impurities in silicon of varying purity has been demonstrated by several experiments. Epitaxial layers grown on gettered mg-Si substrates show properties comparable to those on pure substrates. Experiments on Au doped single crystal demonstrated the effectiveness of the process for fast diffusing impurities. From these results and results on gettered solar cells produced on SILSO substrates, the conclusion is drawn that the a-Si gettering can be a useful process for improving cell parameters when using impure substrates.

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TABLE I. CU, NI AND TI IMPURITY CONCENTRATIONS IN THE SUBSTRATE AND THE EPITAXIAL LAYERS

ELEMENT	CONCENTRATION IN MG-SI [PPMA]	$N_i(x) \times 10^{17} \text{ [cm}^{-3}\text{]}$ IN EPITAXIAL LAYERS $10_{\mu\text{m}}$ AND $25_{\mu\text{m}}$ FROM SUBSTRATE SURFACE AS CALCULATED FOR TYPICAL GROWTH CONDITIONS:					
		(1) THICK SUBSTRATE		(2) THIN SUBSTRATE		(3) THIN, GETTERED SUBSTRATE	
		$N_i(10)$	$N_i(25)$	$N_i(10)$	$N_i(25)$	$N_i(10)$	$N_i(25)$
Cu	30	15	15	7.4	7.4	-	-
Ni	300	140	120	74	71	-	-
Ti	60	10	0.48	9.3	0.42	9.3	0.42

TABLE II. RESULTS FROM VAN DER PAUW MEASUREMENTS ON MG-SI SUBSTRATES AND EPITAXIAL LAYERS

	SUBSTRATES	LAYERS
$\rho \text{ [}\Omega\text{cm]}$	P - TYPE 0.03	N - TYPE 0.02 - 0.03
$\mu_H \text{ [cm}^2\text{ V}^{-1}\text{ s}^{-1}\text{]}$	50	400 - 450
$ N_D - N_A \text{ [cm}^{-3}\text{]}$	4×10^{18}	$(5 - 7) \times 10^{17}$

TABLE III. COMPARISON OF AMI EFFICIENCIES FOR GETTERED AND UNGETTERED CELLS

RUN NO.	CELL CONFIGURATION	$\frac{L_H}{AM}$		$\eta(AMI)^* \text{ [%]}$
1	$5_{\mu\text{m}}$ N-Si (CVD)	2	C.C	4.1
			G.C	4.8
2	$2.5_{\mu\text{m}}$ N-Si (CVD)	10	C.C	5.6
			G.C	6.3
3	$< 1_{\mu\text{m}}$ N-Si (P-DIFFUSION)	35	C.C	5.9
			G.C	7.0

* WITHOUT AR COATING UNDER SIMULATED AMI CONDITIONS

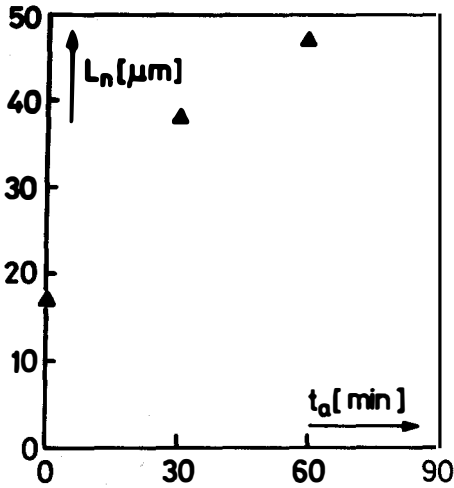


FIG.1. MINORITY CARRIER DIFFUSION LENGTH OF Au DOPED PN-JUNCTIONS AS A FUNCTION OF THE ANNEALING TIME

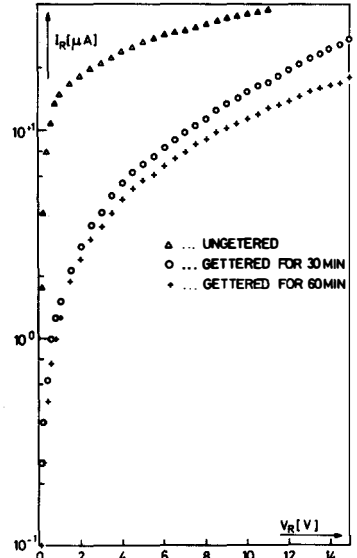


FIG.2 THE INFLUENCE OF α -Si GETTERING ON THE REVERSE BIAS DIODE CHARACTERISTIC OF Au DOPED PN - JUNCTIONS

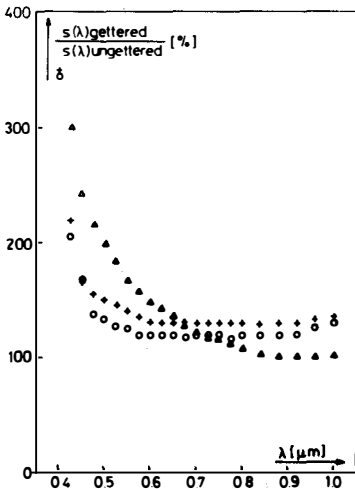


FIG.3 RELATIVE SPECTRAL RESPONSE OF GETTERED CELLS COMPARED TO CONTROL CELLS

- △ ... CORRESPONDS TO RUN 1
 - ◆ ... CORRESPONDS TO RUN 2
 - ... CORRESPONDS TO RUN 3
- IN TABLE III