IMPROVEMENT OF PHOSPHORUS DIFFUSED SILICON SOLAR CELLS BY LASER TREATMENT

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Summary

The most widely used technology for the production of silicon cells is the diffusion of phosphorus into a P-type substrate. However, by this technique, it is nearly impossible to decrease the surface sheet resistance below 35 Ω/□ without degrading too much the spectral sensitivity of the cell. This is due to the fact that the concentration of electrically active phosphorus which can be introduced by diffusion is limited to 4×10^{20} cm^{-3} whereas the total phosphorus concentration may be higher than 10^{21} cm^{-3}. In this work we show that this inactive excess can be partly reactivated by irradiation with short ruby laser pulses of high energy (≃ 1 J/cm^2) which melt the surface of silicon. By this technique sheet resistances as low as 15 Ω/□ could be obtained. A systematic study of this effect and of the influences of the diffusion and irradiation conditions has been performed using SIMS, RBS, electrical and optical methods. An interpretation of the phenomenon in terms of dissolution of precipitates and dissociation of phosphorus vacancies pairs $P^+V^=$ is proposed.

The influence of this treatment on solar cells has also been investigated. A significant increase (≃ 20 mV) of the open circuit voltage has been observed and the efficiency of cells supplied by RTC cell could be improved by about 10 %.

1. INTRODUCTION

The most widely used technology for the production of terrestrial solar cells is the diffusion of phosphorus in a P-type silicon substrate. Since a low series resistance, high open circuit voltage and high spectral sensitivity are required to achieve an efficient device, the resulting N^+ layer has to be as thin and as highly doped as possible. By the classical diffusion procedure, the maximum concentration of electrically active phosphorus which can be introduced is about 2×10^{20} cm^{-3}. This value corresponds to an "electrically solubility limit" which is lower than the total solubility limit since phosphorus in excess may become inactive even if not precipitated due to the formation of vacancy-phosphorus complexes.

Due to these limits and to the particular shape of the P distribution obtained by the diffusion, it is difficult to decrease the sheet resistance below 35 $\Omega/\square$ without degrading too much the spectral sensitivity of the cell by increasing the junction depth and /or forming a dead layer of precipitated phosphorus.

However, a method to decrease the sheet resitance of diffused layers was recently proposed by YOUNG and al [1]. These authors, working essentially on boron diffused samples demonstrated that diffusion induced precipitates can be dissolved by irradiation with high power ruby laser pulses.

In this work we present a systematic study of the effect of similar irradiations with high power ruby laser pulses of energy of 1-2 J/cm^2 on phosphorus diffused layers. The influence of the various diffusion and irradiation conditions have been investigated using SIMS, RBS, electrical and optical methods and an interpretation of the phenomenon in terms of dissolution of precipitates and dissociation of phosphorus-vacancy pairs is proposed. Furthermore, the effect of this treatment on solar cells has been studied and a significant improvement in the performance of a commercial (RTC) solar cell could be obtained.

2. LIMITS OF CLASSICAL DIFFUSION

It is well known that phosphorus can be incorporated into the silicon lattice only if its concentration is lower than the solid solubility limit [2-4]. Phosphorus in excess precipitates [5] and induces misfit dislocations [6].

However, as shown on fig. 1 the maximum concentration of electrically active phosphorus measured by several authors for various diffusions temperatures is lower than the concentration corresponding to the solid solubility limit of P in silicon and does not exceed 2×10^{20} cm^{-3} at usual diffusion temperatures. The existence of this "electrical solubility limit" has been explained recently by TSAI and FAIR [7]. Their model is based upon the idea that phosphorus diffuses into silicon with vacancies in different change states (V^{x}, V^{-} and $V^{=}$). If the concentration of phosphorus is higher than an equilibrium concentration n_e, a significant fraction of the phosphorus atoms is paired with $V^{=}$ vacancies and becomes electrically inactive.

Taking into account the previous limits of the concentration of phosphorus it is possible to calculate the junction depth and sheet resistance of a P diffused layer for various diffusion temperatures and durations. However, due to the complex mechanism of association of P with vacancies, the diffusion law differs considerably from a single erfc. law. Therefore, one has used the semi-empirical analysis of the diffusion proposed by FAIR [8] which takes into account the concepts presented in ref. [7]. Fig. 2 shows the results of such calculations : it appears that if the surface concentration is equal to the solid solubility limit and, if reliable diffusion times (> 10 min) are used, it is nearly impossible to decrease the sheet resistance below 35 Ω/□ without increasing too much the junction depth i. e. degrading the spectral sensitivity of the cell on the short wavelength side. For these reasons, the possibility to decrease the sheet resistance of a diffused layer by a high energy laser treatment demonstrated by YOUNG [1] appeared as a promising way to improve the performance of solar cells.

3. INVESTIGATION OF THE DIFFUSED LAYERS

Samples used in this work were 300 μm thick <111> slices cut from a 1.5 Ω. cm Boron doped CZOCHRALSKY lingot. The diffusion of phosphorus was performed at R. T. C. Caen from a gazeous ($POCL_3$) source at 850 °C for 60 min. The sheet resistance of these layers was measured with a four point probe and was found to be in the range 37-45 Ω/□ . The surface carrier concentration as determined by Hall effect was $\simeq 5 \times 10^{15}$ cm^{-2}. The junction depth was estimated approximately to 4, 000 Å. The dopant profiles were studied by means of the Secondary Ion Mass Spectrometry (SIMS) technique. The apparatus used is a commercial one in which the samples are bombarded with 3 keV Ar^{+} ions and the secondary ions analysed with a quadrupole. The profiles were calibrated in depth with a Talystep and in absolute concentration by means of the Rutherford Backscattering (RBS) technique. The total concentration of phosphorus at the surface was found to be equal to 1–3 $\times 10^{21}$ at/cm^3, which is much higher than the solid solubility limit of P in silicon at the diffusion temperature ($\simeq 6 \times 10^{20}$ at/cm^3 at 850°C according to TRUMBORE [2]). The concentration of electrically active phosphorus was studied by differential sheet resistance measurements by MICHEL [9] and was found to be equal to 2×10^{20} cm^{-3} at the surface. This value fits reasonnably well on Fig. 1 .

The samples were irradiated with short pulses (25–50 ns duration) from a ruby laser ($\lambda = 6943$ Å). The energy density of the pulses could be varied between 0. 8 and 2 J/cm^2. Figure 3 shows that after this treatment the sheet resistance decreases significantly, reaching a minimum value of about 12 $\Omega/\square$ for laser energies higher than 1. 8 J/cm^2. The corresponding increase of the surface carrier concentration is also plotted on the same figure. These results indicate that the concentration of electrically active phosphorus has been increased during the laser treatment. To understand this effect we have to consider the basic mechanism of the interaction of the laser with the semiconductor. It seems well established that for the laser wavelength and energies used here the surface is locally melted. Fig. 4 shows the variation of the depth of the melted zone as predicted by a theoretical model [10]. In the liquid phase the diffusion coefficients of the impurities are very high so that they are redistributed in the melt. After the excitation the crystal regrows , starting from the substrate like in a fast liquid phase epitaxy. Thus, a new dopant concentration profile is obtained which depends on the initial concentration of the impurities, their segregation coefficient, and on the laser energy. The SIMS spectra of Fig. 5 show that the distribution extend over more than 3000 Å if the laser energy density exceeds 1, 4 J/cm^2.

The increase in the concentration of electrically active phosphorus can thus be explained by two effects :

1) During the recrystallization less or no precipitates at all are formed, since the phosphorus is more soluble than during a diffusion because of the strong thermodynamic non equilibrium character of the process. This is confirmed by the RBS spectra of fig. 6, which show that after the laser treatment the concentration of phosphorus atoms on interstitial sites (probably in precipitated form) falls below the detection limits of the method, despite of the fact that the maximum concentration of phosphorus measured by SIMS(fig. 5) remains higher than the solid solubility limit at 850°C.

2) Additionnally less vacancy phosphorus pairs are formed since for the same reasons the equilibrium leading to the formation of these complexes

cannot occur. This is confirmed by the fact that the sheet resistivity can be decreased on samples even if there are no precipitates after diffusion, provided the concentration of phosphorus is higher than the electrical solubility limit.

Thus, the sheet resistance of diffused layers can only be decreased if the layer is doped heavily enough in order that phosphorus precipitates or phosphorus vacancy-pairs are formed. However, it should be pointed out that in our case, after the laser irradiations the maximum concentration of active phosphorus was never higher than $4-5 \times 10^{20}$ cm^{-3} which does not exceed the electrical solubility limit which can be obtained in equilibrium temperatures at 1100°C.

4. EFFECT OF LASER PULSES ON SOLAR CELLS

Solar cells were realised on the previously studied layers. The front grid was obtained by evaporation of 1000 Å of aluminium. The back contact was made by an evaporated layer of gold. Neither antireflective contact nor back field collection were used. I-V measurements were performed under AMI conditions.

Figure 7 shows that both the short circuit current and the open circuit voltage can be improved by the laser treatment. The Voc enhancement can be easily explained by the increase of the concentration of active phosphorus in the N^+ layer. The I_{sc} improvement may be related to the decrease of the sheet resistance, which in our case (non optimal grid spacing) leads to a better collection. The open circuit voltage Voc reaches its highest value (600 mV) for a laser energy of 1.1 J/cm^2 whereas the short circuit current has a maximum (22 mA/cm^2) for 1.45 J/cm^2. Thus the optimal laser energy density is 1.3 J/cm^2. For higher energies both voltage and current decrease probably because of the increased junction depth and of the defects induced by the high energy irradiation. This hypothesis was confirmed by spectral response measurements which showed that the IR response was slightly degraded for these higher energies.

It should be mentionned that the improvement of Voc which can be obtained is relatively more important (20mV) if there is more phosphorus precipitated in the diffusion, i. e. if there is more dopant which can be reactivated.

Since these results were obtained without optimalized grid, antire-

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flective coating and without any back surface field, it was interesting to apply the laser treatment to a commercial solar cell. Therefore a standard R. T. C. cell (Ø 57 mm) was irradiated before deposition of the antireflective coating. The laser energy was 1. 1 J/cm^2. Following results could be obtained under AMI conditions:

I_{sc} (mA)	V_{oc} (mV)	F.F.	η %	R_s (Ω)
710	600-610	0, 75	12, 8	<0, 04

Since the grid spacing is already optimal for sheet resistances of 30-40 Ω/□ the I_{sc} is not improved by the decrease in sheet resistance occuring after the laser treatment. Nevertheless, the high fill factor and open circuit voltage of the cell confirm the high quality of the diode.

CONCLUSION

This work shows that the performance of solar cells can be improved by irradiation with short pulses from a ruby laser. The reactivation of the precipitated and paired phosphorus atoms leads to a decrease of the sheet resistance of the diffusion layer and values as low as 15 Ω/□ have been obtained without increasing the junction depth to more than 4. 000 Å. The optimum open circuit voltage and short circuit current are obtained for laser energy densities of 1. 2-1. 3 J/cm^2. The maximum value recorded for the open circuit voltage is 600 mV which is amoung the highest reported so far.

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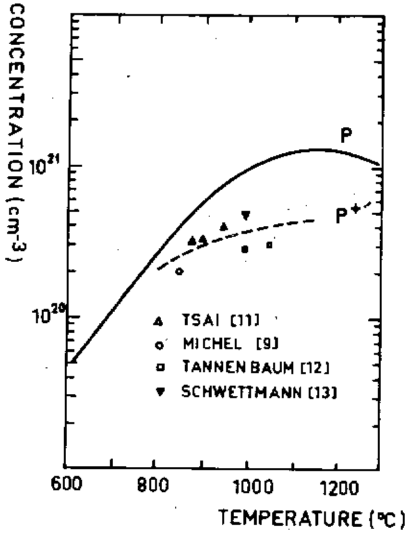

Figure 1

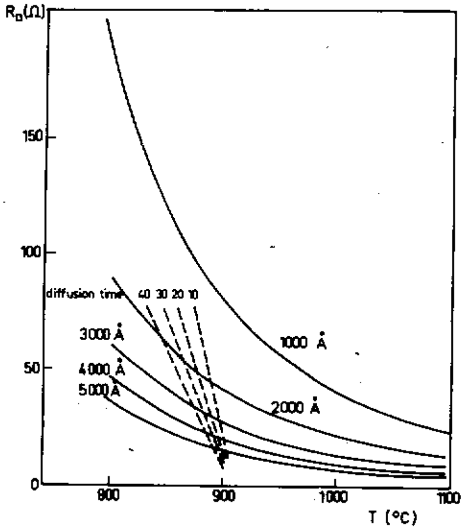

Figure 2

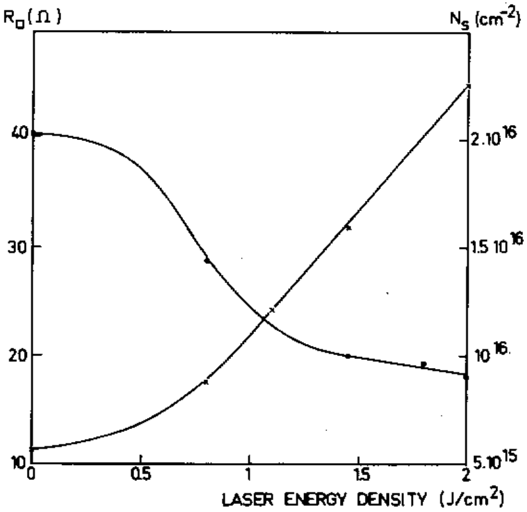

Figure 3

Fig. 1 : Total and electrical solubility of phosphorus.

Fig. 2 : Theoretical relation between sheet resistance, diffusion temperature, diffusion time and junction depth.

Fig. 3 : Sheet resistance and surface concentration versus laser energy density.

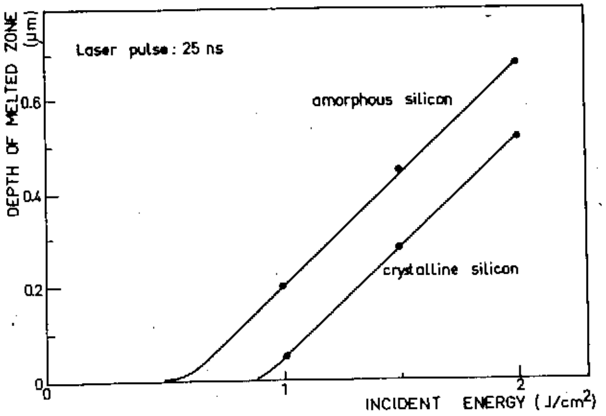

Fig. 4 : Dependence of the calculated melted zone on the laser energy density.

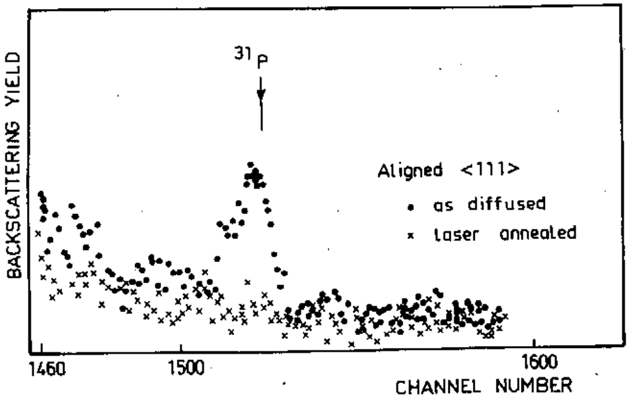

Fig. 6 : <111> aligned backscattered energy spectrum from diffused phosphorus silicon.

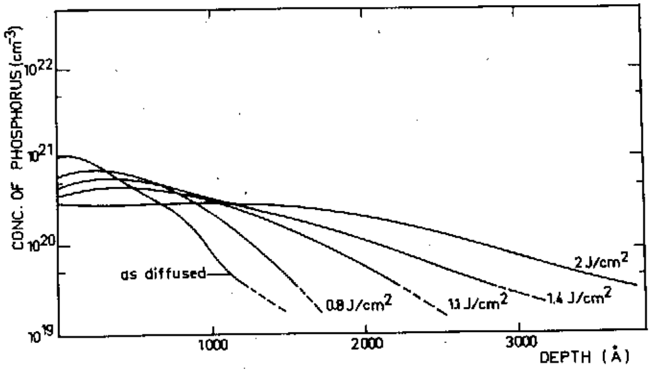

Fig. 5 : SIMS phosphorus concentration profiles for different laser energy density.

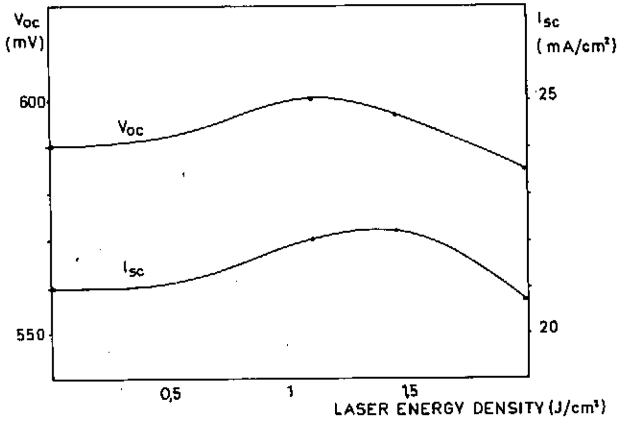

Fig. 7 : Open circuit voltage and short circuit current versus laser energy density.