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LASER TREATMENT OF PHOSPHORUS-DIFFUSED SILICON SOLAR CELLS

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Summary

High energy ruby laser pulses were used to dissolve the precipitates formed during the thermal diffusion of phosphorus into silicon in order to improve the characteristics of diffused solar cells. A maximum V_{oc} of 600 mV and a fill factor of 0.75 were obtained for a laser energy density of 1.1 J cm^{-2}.

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. It is well known that this process must result in an n^+ layer as thin and as highly doped as possible in order to obtain the low series resistance, high open-circuit voltage and high spectral sensitivity required for optimum performance of such devices. Unfortunately the concentration of electrically active phosphorus which can be introduced by diffusion is limited to $(2 - 4) \times 10^{20}$ cm^{-3} since phosphorus in excess of this concentration is inactive not only because of the formation of precipitates when the solid solubility limit is attained [1] but also because of pairing with vacancies [2]. Owing to these limits and to the particular shape of the phosphorus distribution obtained by diffusion, it is difficult to decrease the sheet resistance below 35 $\Omega/\square$ without degrading the spectral sensitivity of the cell too much by increasing the junction depth and/or by forming a dead layer of precipitated phosphorus.

However, a method to decrease the sheet resistance of diffused layers was recently proposed by Young *et al.* [3]. Working essentially on boron-diffused samples these authors demonstrated that diffusion-induced precipitates can be dissolved by irradiation with high power ruby laser pulses.

In this work we applied laser illumination to phosphorus-diffused cells, especially commercial cells, and we determined the power density of the ruby laser that gave the best results. A V_{oc} value of 600 mV was measured for air mass 1 (AM1) conditions, a value which has been reached up to now only for Helios cells [4].

2. Investigation of the diffused layers

The samples used in this work were (111) slices 300 μm thick cut from a 1.5 Ω cm boron-doped Czochralsky ingot. The diffusion of phosphorus was carried out at R.T.C. Caen using a gaseous ($POCl_3$) 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 $\Omega/\Box$. The surface carrier concentration as determined by Hall effect measurements was approximately 5×10^{15} cm^{-2}. The junction depth was estimated to be approximately 4000 Å. The dopant profiles were studied with the secondary ion mass spectrometry (SIMS) technique. A commercial apparatus in which the samples were bombarded with 3 keV Ar^+ ions and the secondary ions were analysed with a quadrupole was used. 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 $(1 - 3) \times 10^{21}$ atoms cm^{-3}, which is much higher than the solid solubility limit of phosphorus in silicon at the diffusion temperature (approximately 6×10^{20} atoms cm^{-3} according to Trumbore [1]). RBS measurements in channelling conditions confirmed that the excess phosphorus was in interstitial sites, probably in precipitated form.

The samples were irradiated with short pulses (25 - 50 ns duration) from a ruby laser (λ = 6943 Å). The energy density of the pulses could be varied between 0.8 and 2 J cm^{-2}. Figure 1 shows that after this treatment the sheet resistance decreases significantly, reaching a minimum value of about 12 $\Omega/\Box$ for laser energies higher than 1.8 J cm^{-2}. The corresponding increase in surface carrier concentration is also plotted in the figure. The results indicate that the concentration of electrically active phosphorus increases 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. 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 as in fast liquid phase epitaxy. Thus a new dopant concentration profile is obtained which depends on the initial concentration of the impurities, their segregation coefficients and the laser energy. The SIMS spectra of Fig. 2 show that the distribution extends over more than 3000 Å if the laser energy density exceeds 1.4 J cm^{-2}. During the recrystallization fewer precipitates or no precipitates at all are formed since the phosphorus is

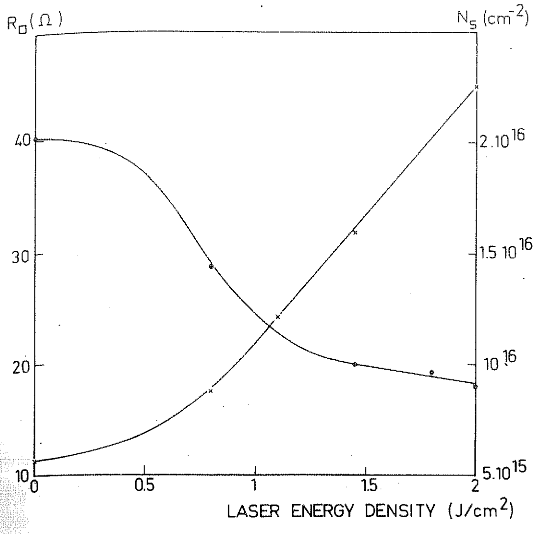

Fig. 1. The sheet resistance (●) and surface carrier concentration (×) as functions of laser energy density.

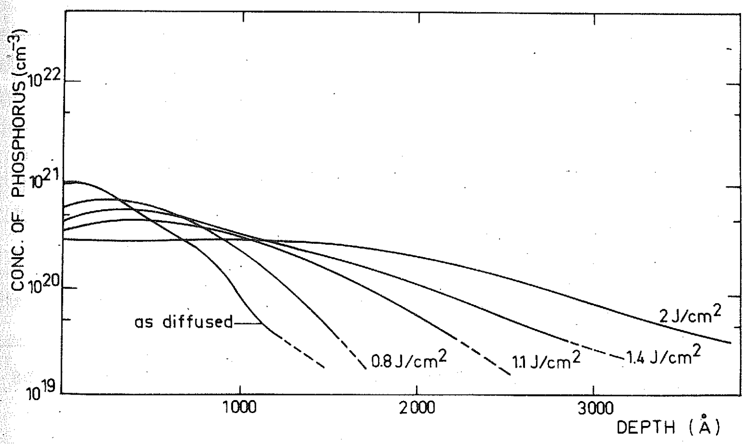

Fig. 2. The SIMS spectra for an as-diffused sample and for samples subjected to various laser energy densities.

more soluble than during diffusion because of the strong thermodynamic non-equilibrium character of the process. This is confirmed by the RBS spectra of Fig. 3 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 the fact that the maximum concentration of phosphorus measured by SIMS (Fig. 2) remains higher than the solid solubility limit at 850 °C. Additionally the dissociation by laser treatment of the $P^{+}V^{2-}$ phosphorus–vacancy pairs formed during the diffusion process also increases the concentration of electrically active phosphorus.

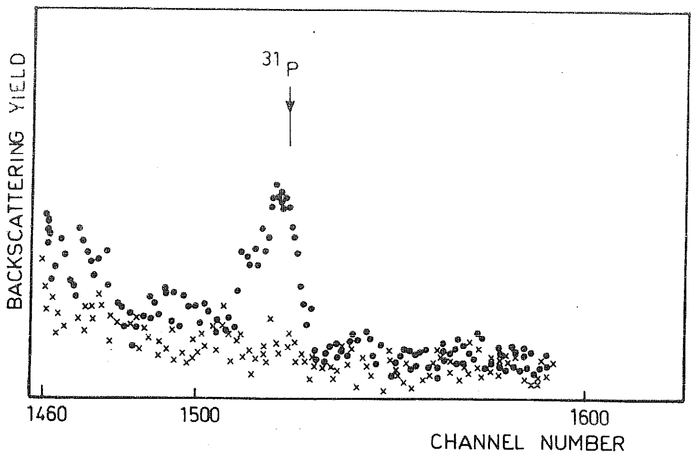

Fig. 3. The RBS spectra aligned along the ⟨111⟩ axis for as-diffused (●) and laser-annealed (×) samples.

This is confirmed by the fact that the sheet resistivity can be decreased even if there are no precipitates after diffusion provided that the concentration of phosphorus is higher than the electrical solubility limit.

3. Effect of laser pulses on solar cells

Solar cells were realized on the previously studied layers. The front grid was obtained by the evaporation of 1000 Å of aluminium. The back contact was an evaporated layer of gold. Neither antireflective contact nor back field collection was used. I–V measurements were performed under AM1 conditions.

Figure 4 shows that both the short-circuit current and the open-circuit voltage can be improved by the laser treatment. The V_{oc} enhancement can easily be explained by the increase in the concentration of active phosphorus in the n^+ layer. The I_{sc} improvement may be related to the decrease in sheet resistance, which in our case (non-optimal grid spacing) leads to better collection. The open-circuit voltage V_{oc} 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 infrared response was slightly degraded for these higher energies.

It should be mentioned that the improvement that can be obtained in V_{oc} is relatively more important (20 mV) 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 an optimized grid, without antireflective coating and without any back surface field, it was interesting

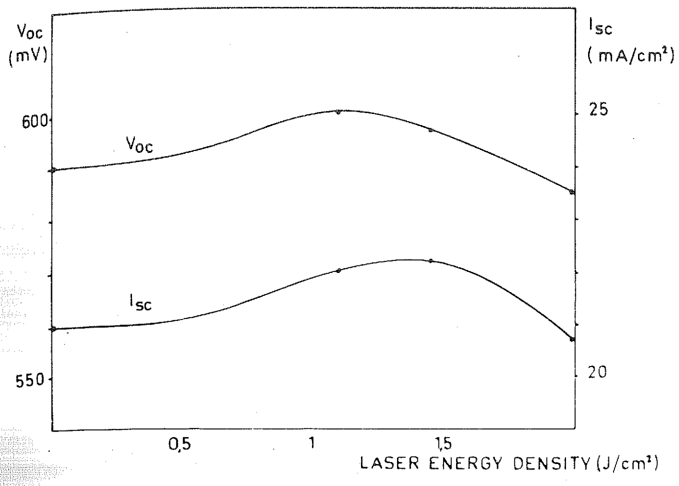

Fig. 4. The open-circuit voltage and short-circuit current as functions of laser energy density.

to apply the laser treatment to a commercial solar cell. Therefore a standard R.T.C. cell (of diameter 57 mm) was irradiated before deposition of the grid and of the antireflective coating. The results obtained under AM1 conditions with and without laser treatment are shown in Table 1. The high fill factor and the open-circuit voltage of the cell confirm the very good quality of the diode.

TABLE 1

	I_{sc}(mA)	V_{oc}(mV)	*Fill factor*	n(%)	$R_S(\Omega)$
Standard	690	590	0.72	11.8	0.06
Laser treated (1.1 J cm^{-2})	710	600	0.75	12.8	0.04

4. Conclusion

This work has shown that the precipitates formed during the diffusion of phosphorus can be dissolved by irradiation with short pulses from a ruby laser. The reactivation of the precipitated phosphorus leads to a decrease in 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 4000 Å. Using this technique the performance of phosphorus-diffused solar cells can be improved; 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 among the highest reported so far.

This technique may have interesting applications for concentration solar cells where low sheet resistances are required and cost limitations are less severe.

References

1 F. A. Trumbore, *Bell Syst. Tech. J.*, *39* (1960) 205.
2 R. S. Fair and J. C. C. Tsai, *J. Electrochem. Soc.*, *124* (1977) 1107.
3 R. T. Young, J. Narayan, C. W. White, J. W. Cleland, W. H. Christie and R. F. Wood, *Proc. IEEE Photovoltaic Specialists' Conf., June 5 - 6, 1978*, IEEE, Washington D.C., 1978, p. 1208.
4 P. A. Payne and R. L. Oliver, *Proc. IEEE Photovoltaic Specialists' Conf., 1976*, IEEE, Washington D.C., 1976, p. 595.