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DOPING OF SILICON WITH ARSENIC AND PHOSPHORUS FROM SPIN-ON SOURCES EXPOSED TO INCOHERENT LIGHT

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Abstract - Short-duration incoherent xenon light exposure has been used to dope silicon single crystals with arsenic or phosphorus from spin-on deposited doped silicon oxide films. Induced temperatures between 1000°C and 1200°C have been applied for exposure times between 10 sec and 30 sec. The diffused layers were characterized by sheet resistivity measurements and Rutherford Backscattering including channeling. Furthermore, solar cells made from these samples were evaluated by spectral response measurements and recording of AM1 current-voltage characteristics. Optimal doping conditions are discussed for arsenic and phosphorus in <100> and <111> oriented silicon single crystals with respect to deposited film thickness, exposure time, and induced temperature.

1. Introduction

Doping of semiconductors by diffusion from doped oxide layers is a well established technique in semiconductor technology1). Usually, the doped oxide layer is deposited on the semiconductor surface by spin-on, and diffusion is accomplished by heat treatment in a furnace at temperatures above 900°C for times of the order of minutes to hours. Recently, high power lasers have been used for doping from surface sources2–4). Typically, laser pulses of some nanosecond duration have been used to melt locally a shallow silicon surface, and the dopants are incorporated into this surface layer by liquid state diffusion. This method is very fast, and diffusion can be confined to selected areas of the wafer surface without affecting the remaining areas. However, due to the small beam diameters available, processing of large areas becomes time consuming5). An alternative approach would be to use short-duration, intense incoherent light to accomplish diffusion from the doped oxide layer. For high dose arsenic implantation in silicon single crystals, significant arsenic diffusion into the bulk has been observed for light exposure times as short as 10 sec6). Thus, diffusion from a doped oxide layer could be expected to take place.

A demonstration of the possibility of doping silicon single crystals with arsenic from a spin-on source exposed to incoherent light has been given in ref.7.
Here we present a more detailed study of this diffusion technique including both phosphorus and arsenic diffusion into silicon single crystals of different crystallographic orientations. Additionally, solar cells made by this technique are characterized.

2. Experimental

The silicon samples used in the experiments were either <100>-oriented, 2 - 5 Ohmcm or <111>-oriented, >5 Ohmcm, p-type (boron doped) crystals. They were 15 x 15 mm² in size, cut from standard one-side polished wafers. Commercial dopant solutions containing either phosphorus or arsenic (Phosphorosilica or Arsenosilica from Emulsitone) were applied to the wafers by spinning, to form either phosphorus or arsenic doped silicon oxide films. The wafers were spun at speeds between 2000 and 3500 rpm for 15 sec to achieve various film thicknesses; this was further achieved by diluting the dopant solutions with ethanol. In this way, doped silicon oxide films of thicknesses between 900 Å and 2800 Å could be obtained as determined by Rutherford Backscattering Spectrometry. Incoherent light exposure of the samples was done by a pre-focused short-arc xenon lamp. A detailed description of this instrument is given in ref.6. The samples were thermally isolated during light exposure, which was performed under normal atmospheric ambient, and the whole sample area was exposed in one step. Subsequently, the samples were treated in dilute HF and rinsed in deionized water, to remove the remainder of the silicon oxide films. Sheet resistivities were then measured with a commercial four-point probe and, in the case of arsenic diffusion, depth profiles and substitutionality in the silicon single crystals were studied by Rutherford Backscattering Spectrometry (RBS), and ion channeling using 2.0 MeV He⁺ ions.

Some of the samples were processed to solar cells by evaporation of aluminum grid patterns through a metal mask. These cells were evaluated by measurements of spectral responses and recording of current-voltage characteristics, as further described in ref.8.

3. Experimental results and discussion

The influence of silicon oxide thickness on dopant diffusion was studied for both phosphorus and arsenic at an induced temperature of 1100°C for an exposure time of 10 sec. Optimal doping, characterized by maximum dopant in-diffusion, as determined by RBS, and minimum sheet resistivity, was obtained, for both dopants, for a film thickness of about 2000 Å, corresponding to a dopant concentration of about 5 x 10¹⁸ at/cm². This film thickness was achieved with the undiluted solutions at a spin-speed of 3000 rpm for 15 sec. The results reported in the following were all obtained with this film thickness.

Figure 1 displays sheet resistivity as a function of exposure time and induced temperature for diffusion into <100> and <111> oriented silicon crystals. It appears that the sheet resistivities obtained for phosphorus diffusion is about a factor of five lower than those for arsenic for similar diffusion conditions. The lowest values, obtained at a temperature of 1200°C for 30 sec, are for phosphorus: 6.7 Ω/□ and for arsenic: 50 Ω/□. At the two highest temperatures investigated, only minor reduction in sheet resistivity is achieved for exposure times longer than 15 sec. There is no difference between the sheet resistivity of the diffused layers in <100> or <111> oriented silicon crystals.

Examples of arsenic concentration profiles determined by RBS are given in Fig.2 for diffusion into <111> and <100> silicon crystals at 1200°C for 30 sec. The profiles extend to a depth of more than 3000 Å having a maximum concentration of about 1 x 10²⁸ at/cm³. The maximum concentration was found to be almost independent of exposure time and temperature whereas the maximum depth was strongly dependent on these parameters (see also ref.7). The total arsenic concentrations determined by RBS were always slightly higher in <111> Si than in <100> Si as can be seen in Fig.3 showing the total concentration as a function of exposure time and induced temperature. However, the additional arsenic in <111> Si is not electrically active as can be deduced from the sheet resistivity measurements (Fig.1). The total arsenic concentrations given in Fig.3 combined with the sheet resistivities
Fig. 1 — Sheet resistivity variation with exposure time and induced temperature for incoherent light induced diffusion of phosphorus and arsenic into <100>- and <111> oriented Si.

From Fig. 1 compare very well to results obtained for arsenic implanted, incoherent light annealed silicon crystals6).

Figure 4 shows examples of backscattering spectra in random and aligned directions from a <100> Si crystal doped with arsenic at 1200°C for 10 sec. The aligned arsenic yield is typical by having a very narrow surface peak of width less than the depth resolution (~300 Å) containing between 5 and 15% of the in-diffused arsenic. The fraction of arsenic contained in this surface peak was found to be about a factor of two higher in <111> Si than in <100> Si. Below this surface peak the sub-

Fig. 2 — Depth profiles from RBS of arsenic in <100> and <111> oriented Si after incoherent light induced diffusion at 1200°C for 30 sec. The drawn curve is not a fit to the profiles.

Fig. 3 — Total arsenic concentration as deduced from RBS after incoherent light induced diffusion into <100>- and <111> oriented Si at the mentioned diffusion conditions.

Fig. 4 — 2.0-MeV He⁺ backscattering spectra in <100> aligned and random directions from a <100> silicon crystal doped with arsenic by incoherent light induced diffusion at 1200°C for 10 sec.
The substitutional fraction was always high, of the order of 90%. The concentration of substitutional arsenic atoms was almost identical for $<100>$ and $<111>$ silicon for similar diffusion conditions in agreement with the measured sheet resistivities (Fig.1), and the additional arsenic concentration in $<111>$ Si compared to $<100>$ Si is contained in the surface peak.

The fraction of arsenic atoms in the spin-on deposited silicon oxide films which has diffused into the silicon crystals (the utilization coefficient) can be deduced from the RBS measurements to be less than 4%. This fraction can also be estimated for phosphorus diffusion by comparing the sheet resistivities given in Fig.1 to sheet resistivities of incoherent light annealed phosphorus implanted silicon crystals. Such a comparison yields total phosphorus concentrations of $1.5 \times 10^{15}$ at/cm$^2$ at $1000°C$, $1.1 \times 10^{16}$ at/cm$^2$ at $1100°C$, and $2.2 \times 10^{16}$ at/cm$^2$ at $1200°C$ for an exposure time of 30 sec. Thus, utilization coefficients as high as 40% can be achieved for phosphorus.

Solar cells were made from a number of samples of both crystallographic orientations and with both of the applied dopants. Since a high surface concentration of the dopant is essential in order to attain a low series resistance and a high open-circuit voltage, arsenic diffusions were carried out at $1200°C$ for 20 sec. Phosphorus diffusions were examined for two different sets of conditions: $1100°C$ for 20 sec and $1000°C$ for 15 sec.

Figure 5 displays typical spectral response curves for phosphorus and arsenic diffused $<100>$ samples. $\eta_{\text{EXT}}$ denotes the directly recorded external quantum efficiency, whereas the internal quantum efficiency, $\eta_{\text{INT}}$, has been obtained by correcting for the measured reflection losses. At short wavelengths the arsenic diffused cell appears superior, due to the rather short penetration depth of the arsenic impurities. However, the high processing temperature ($1200°C$) seems to have left the bulk material with a degraded minority-carrier lifetime, leading to a reduced long-wavelength response, as compared to that of the phosphorus diffused cell processed at $1100°C$. Similar trends were observed for $<111>$ samples, although these cells generally turned out with a long-wavelength response not quite as good as shown in Fig.5.

A significant improvement of the short-wavelength performance of phosphorus diffused cells was obtained by choosing a 15 sec diffusion at only $1000°C$. The very shallow pn-junction resulting from this process led to a 100% collection efficiency already at wavelengths around 400 nm. An attempt was also made to improve the infrared response for some cells by forming a built-in back surface field (BSF). For this purpose, the evaporated aluminium back surface contacts were alloyed in a furnace at $800°C$ for 10 min. Substantial increases of the long-wavelength quantum efficiencies were indeed observed, e.g. up to $\eta_{\text{INT}}>85\%$ at 900 nm. It is not yet clear, however, whether these improvements can be interpreted as a true BSF effect, or merely as a partial restoring of bulk lifetimes degraded during the abrupt xenon-lamp heating.

External quantum efficiencies, as depicted in Fig.5, were integrated with an AM1 solar spectrum, having a total power density of $P_{\text{TN}}=88.92$ mW/cm$^2$, in order to get a measure of the short-circuit current density, $I_{\text{SC}}$. Table I summarizes average results obtained for the different groups of cells. Afterwards, current-voltage characteristics were recorded under illumination from a halogen lamp, calibrated to an AM1-equivalent intensity by means of one of the cells.
Table I - Average values of AM1 short-circuit current-densities. Figures in parentheses for BSF cells.

<table>
<thead>
<tr>
<th></th>
<th>$I_{sc}$ [mA/cm$^2$]</th>
<th>&lt;100&gt;Si</th>
<th>&lt;111&gt;Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>As:</td>
<td>1200°C/20 sec</td>
<td>14.9(16.8)</td>
<td>15.9(16.6)</td>
</tr>
<tr>
<td>P:</td>
<td>1100°C/20 sec</td>
<td>17.2(19.4)</td>
<td>15.8(19.3)</td>
</tr>
<tr>
<td>P:</td>
<td>1000°C/15 sec</td>
<td>19.3</td>
<td></td>
</tr>
</tbody>
</table>

Open-circuit voltages, $V_{oc}$, ranged from 528 to 568 mV for the investigated phosphorus cells and from 503 to 530 mV for the arsenic cells, with a tendency towards the highest values obtained for BSF cells. Fill factors, $FF$, were typically 50 - 55% for the phosphorus cells and were mainly limited by "soft" diode characteristics or shunt resistance, possibly arising from edge effects. For the arsenic diffused cells an additional degradation due to series resistance led to $FF = 40 - 45\%$. The highest resulting AM1 conversion efficiency was found for a low-temperature phosphorus diffused cell (without BSF) and amounted to $\eta = I_{sc}V_{oc}FF/\Pi_{in} = 7.14\%$. With the inclusion of a proper antireflective coating, and supposing a more adequate fill factor, we believe that efficiencies of 15% should be attainable for solar cells made by this new doping technique.

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