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GRAIN BOUNDARY SEGREGATION IN SILICON HEAVILY DOPED WITH PHOSPHORUS AND ARSENIC

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ABSTRACT
Determinations of the grain boundary segregation in polycrystalline silicon films heavily doped with As or P were performed in the temperature range 700-1050°C. It was verified that a significant segregation takes place; the phenomenon is more marked in the case of As, probably due to the excess entropy term. The heat of segregation $\Delta H$ results $\sim$13 kcal/mol, nearly the same for both dopants. The applicability of the models for grain boundary segregation to concentrated solutions is discussed.

INTRODUCTION
The electrical properties of polysilicon are markedly affected by the dopant segregation at the grain boundaries (1,2). The occurrence of this phenomenon for P and As was recently analyzed by Mandurah et al. (3); they showed that, in spite of some crude approximations, the classical model of solute segregation (4) was applicable in the range of conditions explored.

The aim of this work is to study the grain boundary segregation of these dopants in a broader range of conditions, typical of device technology, and to verify whether the simplified model is still applicable although its approximations are justified only for dilute solutions. The fit obtained with the more realistic condition that the fraction of defects positions occupied by the solute is not negligible, is also considered.

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Poly-Silicon films were deposited in a low pressure chemical vapor deposition reactor onto thermally oxidized single crystal silicon wafers. This process was carried out at a temperature of 575°C, a silane pressure of 0.03 Torr, and a deposition rate of 5 nm/min. The thickness of the poly-Si films, of the order of 500 nm, was measured on each specimen with a Talystep; the doping concentration was calculated from the implanted dose divided by the film thickness.

Arsenic and phosphorus ions with doses in the range from $5 \times 10^{15}$ to $5 \times 10^{16}$ cm$^{-2}$ were implanted into the films at an energy of 150 keV. This process was performed with a Lintott III accelerator which provides a doping uniformity better than 2%.

All the specimens were previously annealed at 1050°C in a nitrogen atmosphere for 1h in order to recover the radiation damage, to redistribute the doping into the films, and to stabilize the grain size so that further, lower-temperature, annealing would not change the grain size appreciably.

The average grain size of each composition, after the heat treatment, was determined by transmission electron microscopy (TEM), using the formula suggested by Wada et al. (5).

The specimens were put into thermal equilibrium at different temperatures in the range of 1000-700°C, in steps of 50°C. The annealing experiments were performed in nitrogen atmosphere for times which increased as the temperature decreased, and exactly as follows: 3, 9, 27, 81, 243, 729, and 1500 hrs at 1000, 950, 900, 850, 800, 750, and 700°C respectively. We have verified that these times are sufficient to obtain the equilibrium values of carrier concentration.

The electron concentration and mobility were determined as a function of annealing temperature by resistivity and Hall effects measurements, using the Van der Pauw geometry defined with photolitographic process.

**RESULTS AND DISCUSSION**

The average grain sizes, after annealing at 1050°C the P and As doped poly-Si films at various implanted doses, are reported on the following table:
At low concentrations the grain size is practically the same for P and As doped films, while at the highest dose a marked increase is observed on the grain size of the P doped films. This behaviour is in agreement with previously reported data (6).

The carrier density vs. annealing temperature for the various implanted doses is reported in Figs. 1 and 2 for P and As-doped poly-Si films, respectively. These data clearly show that only a fraction of the dopant is electrically active, and its amount decreases with decreasing temperature. Furthermore, we performed, on a set of samples, annealing at higher temperatures, and verified that these values are reversible and only temperature dependent.

For the lower implanted doses (curves c and d of Figs. 1 and 2), it can be assumed that the electrically inactive dopant was segregated at the grain boundaries.

The phenomenon of the carrier trapping at the grain boundaries (7) can be neglected when we refer to high dopant concentrations. In fact, considering a density of trapping states of about $3 \times 10^{12}$ cm$^{-2}$, the density of carriers trapped

<table>
<thead>
<tr>
<th>Implanted doses (cm$^{-2}$)</th>
<th>Average grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{15}$</td>
<td>0.40</td>
</tr>
<tr>
<td>$1.3 \times 10^{16}$</td>
<td>0.40</td>
</tr>
<tr>
<td>$3 \times 10^{16}$</td>
<td>0.57</td>
</tr>
<tr>
<td>$5 \times 10^{16}$</td>
<td>1.06</td>
</tr>
</tbody>
</table>

Fig. 1 - Carrier density as a function of annealing temperature for poly Silicon films differently doped with P.

Fig. 1 - Concentration des porteurs en fonction de la température pour couches dopé avec P à différentes concentrations.
Fig. 2 - Carrier density as a function of annealing temperature for poly silicon films differently doped with As.

Fig. 2 - Concentration des porteurs en fonction de la température pour couches dopées avec As à différentes concentrations.

at the grain boundaries is very small \(<1 \times 10^{18} \text{ cm}^{-3}\) compared to the total carrier concentration. On the other hand, alternative mechanisms proposed to explain the electrically inactive dopant, like E-centers for P doped samples (8) or clusters for As doped samples are excluded considering our recent results on the solubility and precipitation of these dopants (10-11).

We notice that the carrier concentrations of the heavily doped samples (curves a and b) coincide within the precision of the measurements and are independent of the implanted dose; this phenomenon is due to the occurrence of precipitation (10-11). Moreover the carrier densities correspond, in both cases, to the solubility values previously determined on single crystal specimens (11-12). This finding confirms that the chemical potential of the dopant in the bulk lattice states is not altered by the defect states and by the segregation process.

For the observations of segregation, therefore, we have to take into account only the data of curves c and d, since carrier concentrations are in both cases below the solid solubility in the whole temperature range.

The classical treatment of segregation (13) leads to the formula:

\[
\frac{n_B}{N_B} \cdot \frac{N - N_B}{n - n_B} = \exp\left(-\frac{\Delta F_B}{kT}\right)
\]

where \(N\) is the density of bulk lattice states (in silicon \(\approx 5 \times 10^{22} \text{ cm}^{-3}\)), \(N_B\) that occupied by the solute \(B\), \(n\) is the density of defect states and \(n_B\) that occupied by the solute; \(\Delta F_B\) is the difference in enthalpy between the solute in the defect state
and in the bulk lattice state respectively. It is easy to show that consideration of the excess entropy terms leads to the more complete formula:

\[
\frac{n_B}{N_B} - \frac{N_B}{N - N_B} = \exp \left( \frac{\Delta S_B}{k} \right) \cdot \exp \left( \frac{\Delta F_B}{kT} \right)
\]

where \( \Delta F_B = \Delta H_B - T \Delta S_B \) assumes the meaning of a free enthalpy of binding of the solute B in the defect state. A negative value of \( \Delta F_B \) leads to grain boundary segregation.

This model involves several assumptions and approximations, mainly a single type of defect states and an ideal behaviour of the solvent, which are justified only for very dilute solutions, i.e. for \( N_B << N \).

Furthermore, if the occupancy of both bulk and defect lattice states is neglected, we obtain the simplified very practical form:

\[
\frac{n_B}{N_B} = n - \frac{N_B}{N} \exp \left( \frac{\Delta S_B}{k} \right) \exp \left( \frac{\Delta F_B}{kT} \right)
\]

which was used by (3). We notice that this simplified formula can be better approximated by a straight line.

We report in Fig. 3 our experimental data for As and P according to the above simplified form. It can be noticed that in both cases the fitting with a straight line is better for the dilute solution (curve d). An increase of the solute concentration results in a positive curvature. The occurrence of this phenomenon, which depends on the inadequacy of the model, is clearly evidenced owing to the broader
temperature range explored in our experiments. Due to this effect the absolute values of the binding enthalpy \( \Delta \tilde{h}_B \) turn out to be higher than those determined by (3) in a narrower temperature range.

On the other hand, if the occupancy of the defect states is considered, \( n \) becomes an adjustable parameter. It was observed that a fit, comparable to that in Fig. 3, is obtained by using a value of \( n \) which corresponds to a density of 4-5 defect positions for each lattice position on the boundary. This value is in principle acceptable but its physical significance has to be considered with caution due to the limits of the model. In addition, by using this more realistic formula, the resulting values of \( \Delta \tilde{h}_B \) turn out to be higher than those reported in Fig. 3; in the case of the more dilute solutions they are 0.57 and 0.56 eV for As and P respectively. These binding entalpies do not differ appreciably, as it was formerly pointed out by (3), but the preexponential factor is higher in the case of As, if all other conditions are equal. This is an indication that the larger grain boundary segregation of As is due to the excess entropy term, which is included in the preexponential factor.

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REFERENCES