Redistribution of implanted species in polycrystalline silicon films on silicon substrate

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Abstract. Redistributions of implanted species after thermal annealing in polycrystalline silicon (poly-silicon) were studied by secondary ion mass spectrometry. Ten different elements were implanted into poly-silicon films grown on Si substrates. The implanted energies were chosen such that the expected ion range is within the poly-silicon film. Thermal anneals were carried out at temperatures between 300°C and 1000°C in flowing high purity Ar gas. Three different diffusion behaviors have been observed for these elements. For Be, Na, Ga, and Cr, most of the implanted ions diffused out to the surface of the poly-silicon film after anneal at 1000°C. For K, Ca, Ti, and Ge, the impurity ions diffused deeper into the bulk after anneal at 1000°C. For Cl and Mn ions, the concentration distributions became narrower when annealed at high temperatures.

Introduction

Poly-silicon in recent years has gained importance due to its wide spread applications in solar cell devices, thin film transistors, and gate electrodes [1]. Particularly for the solar cell industry, with a double digit annual growth rate in the last few years [2], the feedstock of solar cells has shifted from the electronic grade silicon scrapes (or rejects) to poly-silicon thin films or wafers. Diffusion of elements into silicon has been extensively studied. However, unlike crystalline silicon, poly-silicon (also known as multi-crystalline silicon) has been much less studied. There is a need to measure the diffusion coefficients of various impurities in poly-silicon for device simulation and modeling [3].

There have been a few reports on the diffusion of impurities in poly-silicon. The diffusion of boron and phosphorus from oxide into poly-silicon has been studied by Kamins, Manoliu, and Tucker [4]. They found that both boron and phosphorus diffused more rapidly into poly-silicon than into single crystalline silicon. They attributed this enhanced diffusion to grain boundary diffusion. Later Hwang et al [5] measured the grain boundary diffusion of Al in poly-silicon films by an Auger sputter profiling technique. They found that the grain boundary diffusion satisfied an Arrhenius-type equation, with $D_b^* = 1.3 \times 10^7 \text{ cm}^2/\text{s}$ and $Q_b = 2.64 \text{ eV}$. This is several orders of magnitude higher than the intrinsic diffusion of Al [6] in single crystalline silicon. Tseng et al [7] on the other hand, studied the diffusion of F in poly-silicon films after implantation of F or BF$_2$. They found that F atoms were attracted to the poly-silicon/SiO$_2$ interface as the annealing temperature increases. The F distribution also narrowed after thermal annealing. They attributed both phenomena to the low solubility of F in Si and to grain boundary diffusion. Chen et al [8] obtained very similar results regarding the distribution of F near the Poly-silicon/Si interface. In 1995, Park and Schroder [9] determined the diffusion coefficient of Cr in edge-defined film-fed-growth poly-silicon to be $2 \times 10^{-17} \text{ cm}^2/\text{s}$ at room temperature. They used Deep Level Transient Spectroscopy (DLTS) measurements to reveal that the grain boundaries are the main sources of
deep-level impurities in the poly-silicon. Nakayama and Sakai [10] reported the redistribution of implanted N in poly-silicon and the segregation of N at the poly-silicon/SiO2 interface and also at the SiO2/Si interface. Michell et al [11] reported the Ge diffusion constant in poly-silicon. They found that it can be described by an Arrhenius relationship with a pre-exponential factor of $D_0 = 0.026 \text{ cm}^2/\text{S}$ and an activation energy of $2.59 \pm 0.36 \text{ eV}$.

Diffusion data are typically obtained from heat treatments of a deposited film on the surface of the material of interest. Use of ion implantation permits the study of any element, and the concentration and depth of the implanted contaminant can be changed by varying the implanted dose and implant energy. Here we report the diffusion behaviors of ten different elements: Be, Na, Cl, K, Ca, Ti, Cr, Mn, Ga, and Ge implanted into poly-silicon thin films grown on silicon substrates.

### Experimental Procedures

The poly-silicon film was grown on a p-type B doped silicon wafer, using a low-temperature chemical vapor deposition technique [1]. The nominal thickness of the poly-silicon film is about 0.5µm. Impurity ions were implanted into this 0.5 µm poly-silicon thin film at room temperature. The implantation energy and dose were tabulated in Table 1. Thermal anneals were carried out in a tube furnace at temperatures from 300°C to 1000°C, for 30 minutes each. Details of the annealing procedures have been reported previously [12-14].

<table>
<thead>
<tr>
<th>Element</th>
<th>Energy (keV)</th>
<th>Dose (atoms/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>70</td>
<td>1E14</td>
</tr>
<tr>
<td>Na</td>
<td>70</td>
<td>1E14</td>
</tr>
<tr>
<td>Cl</td>
<td>150</td>
<td>5E14</td>
</tr>
<tr>
<td>K</td>
<td>150</td>
<td>1E14</td>
</tr>
<tr>
<td>Ca</td>
<td>150</td>
<td>1E14</td>
</tr>
<tr>
<td>Ti</td>
<td>150</td>
<td>1E14</td>
</tr>
<tr>
<td>Cr</td>
<td>120</td>
<td>1.1E15</td>
</tr>
<tr>
<td>Mn</td>
<td>150</td>
<td>1.1E14</td>
</tr>
<tr>
<td>Ga</td>
<td>180</td>
<td>8E13</td>
</tr>
<tr>
<td>Ge</td>
<td>180</td>
<td>4.2E14</td>
</tr>
</tbody>
</table>

Secondary Ion Mass Spectrometry (SIMS) was used to obtain depth profiles of the implanted species in poly-silicon films. The SIMS characterization was carried out at the UCF/Agere Materials Characterization Facility with a CAMECA IMS-3f using 100 nA O2⁺ primary beam at a source potential of 10 kV, an impact energy 5.5 keV, and an impact angle 40° from normal. The focused primary beam of oxygen ions was rastered over a $200 \times 200 \mu$m² or $250 \times 250 \mu$m² areas, with detection of ions from an area of 60 µm diameter at the center of the raster. The sputtering rate is approximately 0.6 nm/s. The depth scale was established for each profile by measuring the crater depth with a stylus profilometer (Sloan Dektak IIA). The concentration of ions was calibrated with the implantation dosages of the as-implanted samples and the measured erosion rate.

### Results

In Fig. 1, we present the SIMS profiles for Be, Na, Ga, and Cr after anneals at different temperatures. For Be, the main features of the SIMS profile are: (1) the trapping of Be atoms at the poly-Si/Si interface, and (2) the out-diffusion of Be atoms at 900°C and above. After 700°C anneal, the Be profile for the top 400 nanometers already showed a flat distribution. For Na ions, the annealing behavior is very similar to that of the Be ions, but the Na traps at the poly-Si/Si interface.
seems to be more stable than the Be traps. Ga and Cr do not seem to have traps at the interface and most of the Ga and Cr atoms left the poly-Si after anneal at 900 °C or above.

Figure 1. SIMS profiles of: (a) $^{9}$Be (70 keV, 1E14 atoms/cm$^2$), (b) $^{23}$Na (70 keV, 1E14 atoms/cm$^2$), (c) $^{69}$Ga (180 keV, 8E13 atoms/cm$^2$), and (d) $^{52}$Cr (120 keV, 1.1E15 atoms/cm$^2$): (●) as implanted, (▲) 500°C, (Δ) 700°C, (×) 900°C, (■) 1000°C.

Figure 2 shows the SIMS profiles for K, Ca, Ti and Ge after anneal at different temperatures. The main feature of the profiles after anneal is that these atoms diffuse deeper into poly-silicon as
annealing temperature is increased. Except for the Ge, the poly-silicon/Si interface acts as a trap for the impurity ions. From the phase diagram of germanium-silicon [15], Ge is fully miscible with silicon, which may explain why there are no traps at the interface for Ge. From the data presented in Figure 2, diffusivities can be extracted through a least square fitting procedure. The results of the fit are listed in Table-2 and discussed in the next section.

Figure 3 shows the SIMS concentration profiles of Mn and Cl after thermal anneal. The main feature in these two profiles is the narrowing of the concentration profiles after anneal. For the Cl case, the poly-silicon/Si interface at 410 nm provided traps for Cl atoms. The as-implanted sample showed a factor of 20 increase in the Cl concentration at the poly-Si/Si interface as compared with the background. After 700°C anneal, the Cl concentration peak at 180 nm becomes much broader. After 900°C and 1000°C anneals, the concentration near the surface (20 nm to 150 nm) was severely depleted, causing the concentration gradient to become even larger than the as-implanted sample. Tseng et al [7] has shown that the narrowing of Fluorine profile under anneal can be explained by grain boundary diffusion based on networks. Our results showed that the diffusion of Cl atoms was very similar to that observed for F atoms.

In Figure 3(b), the SIMS profiles of Mn after anneal at different temperatures are shown. After 700°C anneal, the Mn concentration peak shifted slightly toward the surface and the distribution becomes much narrower. After 900°C anneal, the Mn concentration peak shifted appreciably toward the poly-silicon/Si interface and the distribution also became narrower. But this time the change in the Mn concentration was mainly caused by the depletion of Mn atoms near the surface region. After 1000°C anneal, almost all Mn atoms diffused out of poly-silicon host. The behavior of Mn atoms in poly-silicon is very complex. We will discuss this subject in the next section.

**Discussion and conclusion**

Grain boundaries play an important role in the impurity diffusion in poly-silicon. They are highly disordered regions of finite thickness between ordered microcrystalline crystals. These disordered regions can act either as open conduits for atomic transport and can enhance the impurity diffusion, or they can act as traps for impurities to cause silicide formation and therefore impede the impurity diffusion. As a result, the impurity diffusion in poly-silicon can be a very complex phenomenon as shown in our experiments. As we can see in Figure 1, for Be, Na, Ga, and Cr, the ions eventually diffused to the surface after high temperature annealing. It is known that Be [16] is one of the few metals that does not form silicide, therefore Be diffused out of silicon after anneal at high
temperatures, 900°C and 1000°C. For Na ions, there was one report on the recrystallization and diffusion for Na implanted into single crystalline silicon by Wang et al [17]. They used Rutherford backscattering spectrometry to study the migration of Na atoms and the recrystallization of the amorphous silicon caused by high dose implantation. They found pronounced Na segregation near the amorphous/crystalline interface. After further annealing, this Na segregation dissolved by grain boundary diffusion towards the surface. Our results in Figure 1(b) showed very similar behaviors, including the trapping of Na near the poly-silicon/Si interface and out-diffusion of Na through the grain boundary at high annealing temperatures. At 1000°C, there is still Na trapped at the poly-silicon/Si interface and at the end-of-range (EOR), between 200-300 nm. For Ga ions, the situation is more complex. Linnebach [18] has shown that solubility of Ga in silicon changed from retrograde solubility at temperatures above 630°C to a non-retrograde solubility at temperature below 630°C. This may explain our results that at low temperature the Ga ions tempt to diffuse deeper into poly-silicon, while at high temperature Ga ions tempt to diffuse out of the silicon. Namely there is a competition between the surface desorption and diffusion in the grain boundary: at low temperature, Ga ions desorb slowly, while the diffusion in the grain boundary is relatively fast, at high temperature, the Ga ions desorb quite fast from the surface and Ga does not have time to diffuse into the bulk. For Cr ions, we can compare our present results with our recent work [14] on implanted Cr in single crystalline silicon. We can see that except that in poly-silicon host there is no solid phase epitaxial growth (SPEG). All other aspects of the migration of Cr in poly-silicon are similar to the single crystalline case.

In Figure 2, the K, Ca, Ti, and Ge concentration profiles showed that they more or less stay inside the poly-silicon host. K, Ca, and Ti seem to be trapped by the poly-silicon/Si interface at 500 nm. We used a simple procedure that has been previously documented [19,20]. We assume that the impurity concentration will have a joint half Gaussian distribution and we will only use the concentration profile from the peak to the poly-silicon/Si interface for the calculation of diffusion coefficients. The concentration profile after anneal is given by

\[
C(x) = C_o \exp \left( \frac{-(x-x_m)^2}{2(\sigma^2 + 2Dt)} \right)
\]  

Where \(x_m\) is the peak position and \(\sigma\) is the halfwidth of the as-implanted concentration depth profile. The effective diffusion coefficients of K, Ca, Ti, and Ge were calculated from the plots of the SIMS concentration profiles. The results are given in Table 2. As we can see, while the effective diffusion coefficient of Ge at 700°C in poly-silicon is clearly much larger than that in the crystalline silicon, for K and Ti, the effective diffusion coefficients in poly-silicon are either comparable or much smaller than that in the crystalline silicon.

Table 2. Effective diffusion coefficients at 700°C of K, Ca, Ti, and Ge in Si and poly-silicon.

<table>
<thead>
<tr>
<th>Element</th>
<th>(D) in silicon (from literature)</th>
<th>Reference</th>
<th>(D_{\text{eff}}) in poly-Si (present work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1.3(\times)10(^{-7})</td>
<td>21</td>
<td>6.6(\times)10(^{-15})</td>
</tr>
<tr>
<td>Ca</td>
<td>~</td>
<td></td>
<td>2.1(\times)10(^{-14})</td>
</tr>
<tr>
<td>Ti</td>
<td>3.4(\times)10(^{-13})</td>
<td>22</td>
<td>1.25(\times)10(^{-14})</td>
</tr>
<tr>
<td>Ge</td>
<td>2.7(\times)10(^{-22})</td>
<td>21</td>
<td>3.3(\times)10(^{-16})</td>
</tr>
</tbody>
</table>

The migration behaviors showed in Figure 3 can not be understood through a simple diffusion model. The interaction between the damages and defects created by ion implantation and the formation of silicide need to be considered.
Summary

The redistribution of concentration profiles of ten different elements implanted into poly-silicon films grown on a silicon substrate was studied by SIMS. We found that the annealing behavior of the implant concentration profiles in poly-silicon were very complex. The grain boundary can either enhance the diffusion or it can provide gettering sites to trap the impurities at the grain boundary.

References