STRUCTURAL STUDY OF Si SAMPLES, BEAM CRYSTALLIZED USING MEDIUM ENERGY ION SCATTERING

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The surface structural changes of silicon implanted with heavy ions and ion beam crystallized have been studied by medium-energy ion scattering spectroscopy (MEIS). A toroidal electrostatic analyzer of enhanced energy resolution has been used to detect the scattered ions of a medium-energy He ion beam. Depth profiling results using this technique are compared with those of glancing-angle Rutherford backscattering/channeling (RBS/C) spectra obtained by 1.8 MeV He ions. The dynamics of heavy ions during the ion beam induced epitaxial crystallization (IBIEC) of the implanted amorphous layer as a function of annealing dose was investigated. High depth resolution allows us to track the movement of the implanted species and the crystalline-amorphous (c-a) interface during the beam irradiation. The significant influence of implanted heavy ions on the crystallization process during the subsequent beam annealing is discussed. These results give us deeper insights on IBIEC.

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1. Introduction

Ion beam induced epitaxial crystallization (IBIEC)\textsuperscript{[1]} is the non-equilibrium process at very lower processing temperatures (200–400 °C). Its unique features, such as lower activation energies, less orientation/dopant dependence and low temperature processes compared with the solid phase epitaxial growth (SPEG) are attractive in fabricating semiconductor devices. The activation energies of such ion induced epitaxy were measured to be around 0.3 eV, which is one order of magnitude lower than that of conventional thermal epitaxy (2.7 eV)\textsuperscript{[2]}. The presence of impurities in the amorphized layers may significantly affect the recrystallization behavior, depending on the impurity element and its concentration. All impurity elements used in the present study have very low solid solubility in Si and, for the dose used of $1 \times 10^{15}$ cm$^{-2}$, the Pb and Bi concentrations greatly exceed the solid solubility limits in Si. These species are characterized by very low diffusion coefficients and they are immobile in the time-temperature windows used in IBIEC experiments. Their profiles, therefore, have to remain frozen in the crystalline phase as the crystalline-amorphous (c-a) boundary passes through. In this way, it is possible to produce non-equilibrium structures with impurities trapped in crystalline Si (c-Si) at concentrations well above their solid solubility. Ion implantation of insoluble elements can be used to produce well-defined three-dimensional buried layers with a high volume concentration of implanted elements.

In the present work, we use medium energy ion scattering (MEIS) to investigate the evolution of the depth profiles of the implanted heavy ions in silicon during IBIEC. Rutherford
backscattering spectroscopy (RBS) with a conventional solid-state surface-barrier detector (SSD) was also used for comparison.

2. Experimental details

(100)-oriented, (p-type, 17 Ω cm) silicon wafers were amorphized with 100 keV Pb⁺ and Bi⁺ ions at liquid nitrogen temperature (LNT). In both cases, the implantation dose was 1×10¹⁵ cm⁻². Before the irradiation for beam-induced crystallization, pre-annealing was performed at 450 °C for 1 h in vacuum, to obtain sharp crystalline-amorphous (c-a) interfaces. A thin oxide layer of 56 Å SiO₂ was formed on the Si surface during this pre-annealing treatment, as measured by a SOPRA ES4G rotating polarizer spectroscopic ellipsometer. These processes resulted in an amorphous layer at the surface, with a thickness of 730 Å for Bi or 760 Å for Pb [3]. Irradiation with 3 MeV Si⁺ ions from a 3 MV tandem was used to stimulate IBIEC. The beam current density was 0.075 μA cm⁻² and the doses were 5×10¹⁴, 1×10¹⁵, and 2×10¹⁶ cm⁻². The total energy deposition at the depth of the initial c-a interface was 120 eV/atom for the highest dose used, and is nearly constant within the range of the measured depth. The temperature rise of the irradiated area was negligible, and the sample holder temperature was stabilized at 400 °C (± 2 °C).

RBS measurements were performed using a 1.8 MeV He⁺ beam from a Van de Graaff accelerator in glancing angle geometry at 100°. A silicon surface-barrier detector was used, with an overall resolution of about 15 keV FWHM. To achieve better depth resolution, MEIS measurements were performed using a 125 keV energy He⁺ beam from a 400 kV Cockcroft accelerator. A toroidal electrostatic analyzer (TEA), installed in a vacuum chamber at 9×10⁻⁵ Pa, was used for MEIS measurements. The overall energy resolution of the MEIS system was 0.5 keV for the energy used. The scattered ions were detected at a scattering angle of 120° with an angle of acceptance of ± 2.5°. Energy calibrations were performed using 200 Å Au on Si and bulk SiO₂ samples. Depth distributions of both vacancies and implanted atoms were calculated by SRIM [4].

3. Results and discussion

The energy and depth resolutions of conventional RBS and the MEIS-RBS were calculated using Ziegler’s stopping power values [4]. Two scattering angles (165° and 100°) were assumed in the case of conventional RBS.

![Fig. 1. Calculated energy resolution (a) and depth resolution (b) for conventional RBS (165° and 100°) and RBS/MEIS (120°) systems as a function of target depth.](image)

Fig. 1(a) shows the calculated energy resolution of the two systems as a function of target depth. In conventional RBS, for a depth of 0-60 nm, the energy resolution (15-18.6 keV) is dominated by that of the SSD (15 keV). On the other hand, the resolution of MEIS is much better (0.5-3.5 keV), because the energy resolution of TEA is only 0.5 keV in the case of 125 keV He⁺.
the case of conventional RBS, the energy resolution at a 100° scattering angle is 3 keV higher than that at 165° for a depth of 60 nm. This is because of Bohr straggling during the added path lengths of the scattered ions. Fig. 1(b) shows the calculated depth resolution, using the energy-loss factor. The effect of a glancing detecting angle (100°) is well-pronounced in the conventional RBS. The depth resolution is 8.5-10.5 nm, greatly superior to that of 165° (32.3-33.9 nm). Better depth resolution could be obtained by MEIS, due to the much better energy resolution of TEA. The depth resolution of 1.0-7.6 nm is superior to that of conventional RBS at a glancing detecting angle of 100°. At the surface of the investigated sample, the difference in the depth resolution for the two systems is large and becomes less in the deeper region. These calculations clearly indicate the outstanding capabilities of MEIS in combination with the enhanced energy resolution of TEA.

![Fig. 2](image)

Fig. 2. Random spectra of the Pb-implanted samples after IBIEC obtained with conventional RBS, 1.8 MeV He⁺ beam at glancing angle (100°) (a) and RBS/MEIS, 125 keV He⁺ beam at 120° scattering angle (b).

Fig. 2(a) shows glancing-angle (100°) RBS spectra of samples implanted with Pb before and after irradiation with 3 MeV Si at various annealing doses. The Pb distribution and the Si edge are clearly seen in all spectra. Massive redistribution of the initially formed Pb profile in a-Si occurs when the c-a interface passes through it under IBIEC. With increasing annealing dose, the initial peak begins to move to the surface. The detected peak widths are close to the resolution of the measuring system, so that the measured spectra are presumably broadened. An analysis technique of further enhanced depth resolution is required to profile the exact Pb distributions. Fig. 2(b) shows the MEIS spectra of the Si samples implanted with 100 keV Pb⁺ ions at 1x10¹⁵ cm⁻² and beam annealed with 3 MeV Si⁺ at three doses. As a measure of the thickness of the resulted peaks in this paper, we use the full width at half maximum (FWHM). The annealing conditions, resulting thickness measured from the spectra, and the theoretical calculations are summarized in Table 1.

![Table 1](image)

Table 1. Summary of the annealing conditions and the results for the FWHM obtained by MEIS.

<table>
<thead>
<tr>
<th>Projectile ion</th>
<th>FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as-implanted</td>
</tr>
<tr>
<td>Pb</td>
<td>25.5</td>
</tr>
<tr>
<td>Bi</td>
<td>24.1</td>
</tr>
<tr>
<td></td>
<td>20.5</td>
</tr>
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</table>

The FWHM of the as-implanted sample is 24 nm, close to the theoretically predicted value of 25.5 nm by SRIM. The maximum concentration of this Pb profile occurs 43.8 nm beneath the Si surface, which is again in very good agreement with the value of 45.5 nm calculated by SRIM. With increasing Si dose, the peak width (FWHM) narrows. The asymmetric shape of the Pb peak in the case of 1x10¹⁶ cm⁻² is ascribed to non-uniform crystallization caused by the high concentration of Pb...
atoms. Close observation of the two spectra for $1 \times 10^{16}$ cm$^{-2}$ and $2 \times 10^{16}$ cm$^{-2}$ indicates that the Pb concentration below the peak (at a depth < 15 nm) increased with increasing annealing dose from $1 \times 10^{16}$ cm$^{-2}$ to $2 \times 10^{16}$ cm$^{-2}$. It seems likely that during the final annealing dose (2x$10^{16}$ cm$^{-2}$) the c-a interface reaches the surface and Pb atoms start to diffuse back to the bulk side. A resulting peak width of 3.5 nm was formed at the Si surface. The insufficiency of Si at the Si edge (i.e. a shift of the Si edge to lower energy) confirms the surface segregation of Pb.

Fig. 3. Random spectra of the Bi-implanted samples after IBIEC, obtained with (a) conventional RBS. 1.8 MeV He$^+$ beam at a glancing angle (100$''$), and (b) RBS/MEIS, 125 keV He$^+$ beam at a 120$''$ scattering angle.

The crystallization process after IBIEC of Bi implanted Si (Figs. 3(a) and (b)) is different. The FWHM of the as-implanted sample is 20.5 nm, close to the value of 24.1 nm theoretically predicted by SRIM. The maximum concentration of this profile occurs 41 nm beneath the Si surface, which is in a good agreement with the value of 44.9 nm calculated by SRIM. After the first dose of annealing (i.e. 5x$10^{15}$ cm$^{-2}$) the implanted Bi species move slightly to the surface. With increasing IBIEC doses, the profile remains unchanged in the crystalline phase as the c-a boundary passes through. Massive redistribution of the implanted Bi (in- and out-diffusion) occurs at the highest annealing dose of $2 \times 10^{16}$ cm$^{-2}$. The simulation of this spectrum shows that during this redistribution, Bi cannot reach the Si surface and segregate at the interface between the thin native oxide and the silicon substrate. As in the case of Pb, here one can see an insufficiency of Si near the Si edge, clearly indicating Bi segregation in the near-surface region. The very good depth resolution of MEIS allows us to follow in detail the evolution of the implanted Pb species during IBIEC. Conventional RBS could not provide such unique information.

4. Conclusions

Two analysis techniques, MEIS and conventional RBS, have been applied to investigate the evolution of Pb and Bi species, implanted into Si and ion beam annealed with 3 MeV Si$^+$. A massive redistribution of the initially formed profiles was observed. This study could provide a quantitative description of the formation of the near-surface peaks in Si during IBIEC. A detailed MEIS study was able to give unique information on the beam-induced crystallization process in silicon.

References