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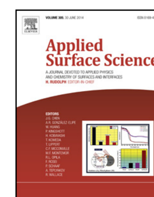

Loss of implanted heavy elements during annealing of ultra-shallow ion-implanted silicon: The complete picture

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From the observations of the annealing process of ultra-shallow Sn and Pb implanted Si, we propose the mechanism and the triggering conditions for the dopant dose loss effect commonly observed in heavy ion-implanted silicon. The results of high-resolution Rutherford backscattering spectrometry, high-resolution cross-sectional transmission electron microscopy and Monte Carlo simulations are presented. With these results, we construct a complete chain of events that leads to the loss of most of the implanted ions. First, the implanted atoms agglomerate into liquid melts during high temperature electron beam annealing, causing polycrystalline phase formation. Next, liquid phase movement takes place along grain boundaries, and the implanted atoms are forced out of the surface layer as the grain boundaries disappear during grain growth, leaving behind low concentrations of residual atoms. The specific conditions that trigger such a sequence of processes are identified.

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1. Introduction

Ion implantation using ion beams is a well-established technique used in many materials systems, e.g. for the creation of novel materials and for dopant introduction in semiconductors at concentrations well above the maximum equilibrium solid solubility. Its advantage lies in its capability for precise tailoring of the concentration and depth profile of the implanted ions, with a strict control of the ion incident energy and fluence. In contrast to commonly used film deposition methods such as chemical vapor deposition (CVD) where the phase of the films (monocrystalline, polycrystalline or amorphous) is determined by the deposition conditions, a subsequent annealing process is required after ion implantation in order to induce crystal regrowth by solid phase epitaxy (SPE). This is important for dopant activation in silicon device manufacturing where implanted atoms (dopants) are required to occupy substitutional sites.

For heavy implanted ions such as In [1], Sn [2,3], Sb [4] and Pb [5,6] in silicon, progressive lattice reconstruction with SPE indeed occurs at implantation doses below a certain threshold dose. However, at implantation doses which exceeds the threshold, polycrystalline phase formation occurs instead of SPE and significant losses of the implanted atoms occur after the grain growth process to the monocrystalline phase. The threshold dose varies for different combinations of implanted atom and substrate elements. Such a dopant dose loss effect presents a serious problem for ultra-shallow junctions, where incomplete activation as well as the loss of implanted In [7] and Sb [8,9] after annealing occurs at high dopant concentrations. Indeed, a recent study of Sb implanted Si [9] revealed that the Sb loss exceeds 80% for an implantation fluence of 1×10^{15} cm^{-2}. Such losses severely limit the usefulness of heavy-ion implantation as a method for creating ultra-shallow junction, heavy-dopant introduction, or band gap engineering of novel materials in Si photonics research. This has since led to research in co-implantations [10,11] in an effort to improve dopant retention during ion implantation. To date, there is no clear picture of what triggers the polycrystalline phase formation and how this is linked to the loss of the implanted ions. A clear understanding of the implanted atom loss process during annealing, as well as the conditions which trigger such a phenomenon, is important for the ongoing heavy-ion implantation research.

Apart from modeling the dopant dose loss effect, the use of Sn and Pb implantations in Si also illustrate the research in Group IV semiconductors, which has potential applications in photonic devices capable of monolithic integration with existing Si devices and platforms [12]. The recent demonstration of direct band gap

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luminescence in Ge for GeSn semiconductor alloys [13] has sparked intense research interest in such alloys. However, the relative scarcity and the high cost of Ge remains an obstacle to future industrial mass production. Nonetheless, the mechanism of the dopant dose loss effect described here is quite likely to also be applicable in heavy-ion implanted Ge.

Modern research now requires the investigation of thin films and junction depths with thicknesses of only several nanometers. Meaningful characterizations must therefore be performed using methods with high depth resolution. High-resolution Rutherford backscattering spectrometry (HRBS) [14] is capable of non-destructive and quantitative elemental profiling with sub-nanometer depth resolution for heavy elements. High-resolution cross-sectional transmission electron microscopy (XTEM) provides high-magnification imaging for identification of the crystalline phase.

In our previous work [15], results showed a progressive advance of the amorphous/crystalline interface in Sn implanted Si samples due to SPE at low implantation fluence. There was no movement of the implanted Sn atoms even at annealing temperatures far exceeding the melting point of Sn, and the implanted region remains amorphous throughout the annealing process. Such a SPE regrowth process is favorable for practical applications as the Sn atoms are retained and they occupy substitutional sites after SPE.

In this work, we present observations on the crystal regrowth process where a transformation to the polycrystalline phase has occurred instead of SPE during the annealing of Sn and Pb implanted Si samples at higher fluences. HRBS, high-resolution XTEM measurements as well as Monte Carlo simulations were performed to determine the characteristics of the grain growth process of the polycrystalline phase within a depth of 50 nm. From the entirety of these results, we construct a complete chain of events that leads to the loss of most of the implanted atoms and identify the conditions which trigger such a chain of processes. This series of phenomena may apply to all heavy-ion implanted samples with low implant element melting point, and is not just limited to Group IV alloys of Si.

2. Experimental

Samples were prepared at GNS Science, New Zealand [16]. Focused beams of heavy ions produced by a Penning sputter ion source from solid materials were scanned across the target surfaces. Identical n-type Si(1 0 0) substrates for all samples were first self-amorphized at room temperature with 25 keV Si^+ ions at a fluence of 5×10^{14} cm^{-2}. For Sn-implanted Si samples, 20 keV Sn^+ implantations were performed separately at fluences of 5×10^{15} and 1×10^{16} cm^{-2}. For cross-sectional TEM analysis, Sn implanted sample at 2×10^{15} cm^{-2} from our previous work is also included in the analysis. For Pb-implanted Si samples, 20 keV Pb^+ implantations were performed at a fluence of 2×10^{15} cm^{-2}. For simplicity, this paper shall refer to 2×10^{15}, 5×10^{15} and 1×10^{16} cm^{-2} as low, medium and high fluence, respectively. Each implanted sample undergo electron beam annealing at temperatures up to 800 °C at 500 s duration. During annealing, a focused 20 keV high current electron beam of 3–4 mA was raster scanned over the sample with temperature gradients of 5 °C s^{-1} during the heating and cooling phases of the annealing cycle. At peak temperature, an accuracy of ±1 °C was obtained using a computer controlled feedback system. Both ion implantation and electron beam annealing are carried out in high vacuum of $\sim 10^{-7}$ mbar.

HRBS measurements were performed at the Centre for Ion Beam Applications at the National University of Singapore [14]. A beam of 500 keV He^+ ions was generated by a 3 MV Singletron accelerator and was collimated to a divergence angle of <1 mrad. The beam was incident on each sample, which was mounted on a high precision 5-axis goniometer within a UHV scattering chamber of $<5 \times 10^{-9}$ mbar. Ions scattered at 65° were analyzed by a 90° double-focusing magnetic spectrometer and were collected by a 100-mm 1-D position sensitive resistive-strip focal plane detector. Our detection system has an energy resolution of ∼1 keV at 500 keV incident beam energy, which allows for sub-nanometer depth resolution for heavy elements. Aligned spectra were measured with the beam travelling along the ⟨111⟩ channeling axis of the Si substrate. High resolution XTEM imaging was performed on sample cross-sections, using a 200 keV JEOL2010F field emission machine.

3. Results: HRBS, XTEM and T-DYN

Fig. 1 shows the HRBS spectra of medium and high fluence samples of Sn implanted Si, respectively. The spectra for individual samples are shown in Figs. A.1, A.2 and A.3 in the Appendix. The as-implanted Sn profile display peak concentrations of 6.4 at% and 11.4 at%, respectively for medium and high fluences, as fitted by the SIMNRA simulation code [17]. Upon annealing, both sets of samples show Sn redistribution, with significant accumulation within a 5 nm depth at the surface. Such an effect is normally undetectable by conventional RBS using solid state surface barrier detectors, due to the lack of depth resolution. The aligned spectra of the Si signal also indicate that crystal regrowth has taken place to a larger extent with increasing annealing temperature accompanied by a corresponding decrease in the depth of Sn redistribution, indicating that SPE and polycrystalline phase formation are competing processes. Both sets of sample achieved the monocrystalline phase during annealing at 800 °C, accompanied by the loss of most of the Sn atoms. However, a broadly distributed, low level of residual Sn remains, situating at mean depths of ∼18 nm and ∼24 nm for medium and high dose samples, respectively.

Fig. 2 shows the high-resolution XTEM images of the Sn implanted Si samples. Fig. 2(a) shows that the low fluence Sn sample from our previous work [15] remains amorphous during annealing at 520 °C, and progressive SPE regrowth occurs. No Debye-Scherrer rings are detected for this sample under diffraction mode. Fig. 2(b) and (c) shows the polycrystalline phase formation for samples at medium and high fluences. A smaller average grain size is seen in the high fluence sample, indicating a lower grain growth rate for higher implantation fluence. The Debye-Scherrer rings are seen in diffraction mode, shown in the inset of Fig. 2(c), confirming the formation of the polycrystalline phase.

Fig. 3 shows the random and aligned HRBS spectra for the low fluence Pb implanted Si samples annealed between 400 and 800 °C. The as-implanted peak Pb concentration is 4.3 at%. At 400 °C anneal, there is yet no movement in Pb and the SPE a/c front is still at a depth of ∼38 nm. By 500 °C, however, most Pb atoms are lost, with the remaining non-crystalline Si signal being roughly half the height of the random level, indicating that the layer is no longer amorphous. By 800 °C, the crystal regrowth is complete, leaving behind residual Pb at two distinct mean depths of ∼25 nm and ∼15 nm. Note that for the 800 °C random spectrum, some slight ion channeling had still occurred, resulting in a lower random Si signal. Our results are in good agreement with previous conventional RBS studies of ion implanted Pb in Si [5,6].

Fig. 4 shows the high-resolution XTEM micrographs for the low fluence Pb implanted Si samples annealed at 400 °C and 600 °C. Results show dark spots distributed over a depth range of 15–21 nm from the surface for the 400 °C sample, which suggests the start of the polycrystalline phase formation. The magnified view in the inset of Fig. 4(a) shows that the spots appear to be small polycrystallites. It is not possible to identify the elemental identity of these crystallites, but we believe these are in fact Si crystallites which

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