Interstitial-type defects away from the projected ion range in high energy ion implanted and annealed silicon

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(Received 22 March 1999; accepted for publication 6 July 1999)

Defects in high energy ion implanted silicon have been investigated, especially in the depth range around half of the projected ion range $R_P/2$ after annealing at temperatures between 700 and 1000 °C. Preferable trapping of metals just in this depth range proves the existence of defects there. No vacancy-like defects could be detected by variable energy positron annihilation spectroscopy after annealing at temperatures $T>800\,^\circ\mathrm{C}$. Instead, interstitial-type defects were observed in the $R_P/2$ region using cross section transmission electron microscopy of a specimen prepared under special conditions. The results indicate the presence of small interstitial agglomerates at $R_P/2$ which remain after high temperature annealing. © *1999 American Institute of Physics.* [S0003-6951(99)03135-6]

Ion implantation is a standard process for the precise and controlled introduction of dopants and other impurities into Si crystals. However, the necessary annealing of radiation damage becomes a problem as the thermal budget is reduced in modern device technology. This especially holds for the implantation of high energy ions. During a typical MeV ion implantation more than 10^3 Si atoms are displaced by collisions along the trajectory of each implanted ion. In the so called ''+1'' model,[1] it is assumed that each implanted atom finally occupies a substitutional lattice site thus replacing the host atom and creating a self-interstitial. The radiation damage, with the exception of one self-interstitial per implanted ion, is completely annealed by a thermal treatment when the temperature rises up to about 800 °C. Subsequent processes during annealing at temperatures $T>800\,^\circ\mathrm{C}$, like the evolution of extended secondary defects and the dopant redistribution, are completely controlled only by the +1 atoms.[2] For keV ion implantation the +1 model is well established and widely applied in process simulating programs.

On the other hand, after MeV ion implantation and annealing in the temperature range between 700 and 1000 °C residual defects have been recently observed by means of metal gettering in two distinct depth regions: around the mean projected ion range R_P and also between the surface and R_P, mainly at $R_P/2$.[3–7] This defect structure occurs for a variety of implants, gettering species, and annealing conditions.[8] It has been assumed that the defects in the $R_P/2$ region are vacancy agglomerates remaining from an excess of vacancies.[5,7,9,10] However, no structural defects have been found up to now in this region by cross section transmission electron microscopy (XTEM).[5,8] The detailed nature of the damage around $R_P/2$, which effectively acts as a gettering center for metal impurities, is not yet known.

In the present study the occurrence of vacancy defects in the $R_P/2$ region has been investigated by variable energy positron annihilation spectrometry (PAS), an analysis method which is sensitive to vacancy-like defects. Moreover, the $R_P/2$ region has been carefully analyzed by XTEM after specimen preparation using ion milling in a ''Gatan Duo Mill 600'' with 4 keV Ar^+ ions of 1 mA total current under an incidence angle of 13°. The experiments were performed on *n*-type (100) CZ–Si and FZ–Si. The substrates were implanted with 3.5 MeV, $5\times10^{15}\,Si^+\,cm^{-2}$ ($R_P=2.7\,\mu$m) and annealed either at 850 °C for 1 h or at 900 °C for 30 s in Ar ambient. It was determined by XTEM that the Si^+ ion implantation does not amorphize the Si lattice. Before annealing, Cu has been introduced into the rear surface of part of the samples by implantation with 20 keV, $3\times10^{13}\,Cu^+\,cm^{-2}$. The Cu depth distribution has been determined after annealing by secondary ion mass spectrometry (SIMS).

The PAS equipment at the Forschungszentrum Rossendorf[11] has been used to check for the existence of vacancy-type defects in the $R_P/2$ region of MeV ion-implanted Si samples without Cu contamination after thermal annealing at 900 °C for 30 s. For these samples metal gettering at $R_P/2$ has been observed if they were contaminated with Cu. The results, presented in Fig. 1, clearly indicate the formation of vacancy-type defects due to ion implantation as the normalized S parameter is $S/S_b>1$ (as-implanted state). Thermal treatment at $T>850\,^\circ\mathrm{C}$, as performed here, should remove these vacancy-type defects. Indeed, the curve measured after annealing at 900 °C for 30 s is almost identical to the curve corresponding to unimplanted material ($S/S_b\leq1$) except close to the surface. This finding is in general agreement with other investigations[5,12,13] demonstrating the disappearance of vacancy-type defects as the annealing temperature exceeds 800 °C. The depth distribution of the vacancy-type defects for the as-implanted state can be assumed to be simply box shaped. The best fit to the measured $S(E)$ data of Fig. 1 has been obtained by the com-

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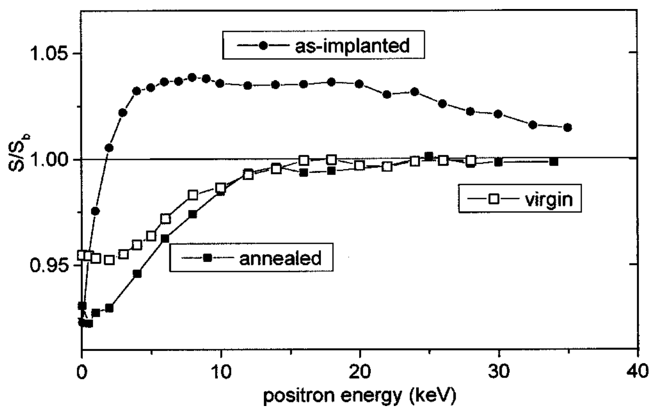

FIG. 1. PAS results showing the normalized S parameter S/S_b vs the positron energy E for Si samples implanted with 3.5 MeV, $5\times10^{15}\,\mathrm{Si}^+\,\mathrm{cm}^{-2}$ (without Cu contamination) in the as-implanted state and after a thermal treatment at 900 °C for 30 s. The $R_P/2$ and R_P region corresponds to $E\sim15$ and 23 keV, respectively. No vacancy defects are detected after annealing ($S/S_b<1$).

puter code VEPFIT[14] for a simple box profile reaching from the surface to a depth of 3.31 μm. The calculated value of $S/S_b=1.037$ indicates that the vacancy-type defects detected in the as-implanted sample are larger than monovacancies, probably divacancies.[15] The ratio S/S_b depends on the energy resolution of the Ge detector used. Data about the size and concentration of these defects could be achieved by depth-dependent positron lifetime measurements.[16] Oxygen precipitates (SiO_2), which possibly form during annealing at 900 °C in vacancy-rich regions,[9] also can influence the S/S_b value.[15,17] However, oxygen precipitates do not appear to form the dominating gettering centers for metals, because oxygen gettering is a competitive process to metal gettering[4] and the $R_P/2$ effect has been found to be stronger for epi-Si containing much lower oxygen concentrations than CZ–Si.[6] Finally it can be stated that for the annealed sample the vacancy defect concentration is below the PAS detection limit of $1\times10^{15}\,\mathrm{cm}^{-3}$.[18] This is about two orders of magnitude lower than the maximum concentration of Cu gettered at $R_P/2$. For this reason vacancy-like defects cannot explain the gettering of Cu in the $R_P/2$ region.

By means of XTEM we discovered interstitial-type defects just in the depth region around $R_P/2$ in samples for which the $R_P/2$ effect was observed by Cu gettering. These defects are loop-like planar defects on (111) planes. Their interstitial character has been analyzed by diffraction contrast. Such dislocation loops have been found in both FZ and CZ material and their density and depth distribution correlates with the Cu depth distribution measured for the same sample. All TEM investigations have been performed for such conditions that the creation of extended defects by the electron beam can be excluded. The sample with the highest average defect density of $6\times10^{13}\,\mathrm{cm}^{-3}$ is presented in Fig. 2 (top) and compared with the corresponding Cu depth profile (bottom). The defects have been found only after thinning the XTEM specimens by ion milling under the conditions mentioned above. They never appeared in samples without MeV ion implantation. The incidence angle of the Ar^+ ions is a crucial parameter for the occurrence of visible defects at $R_P/2$. No defects could be found if the incidence angle was below 10°. Detailed results have been published in Ref. 19.

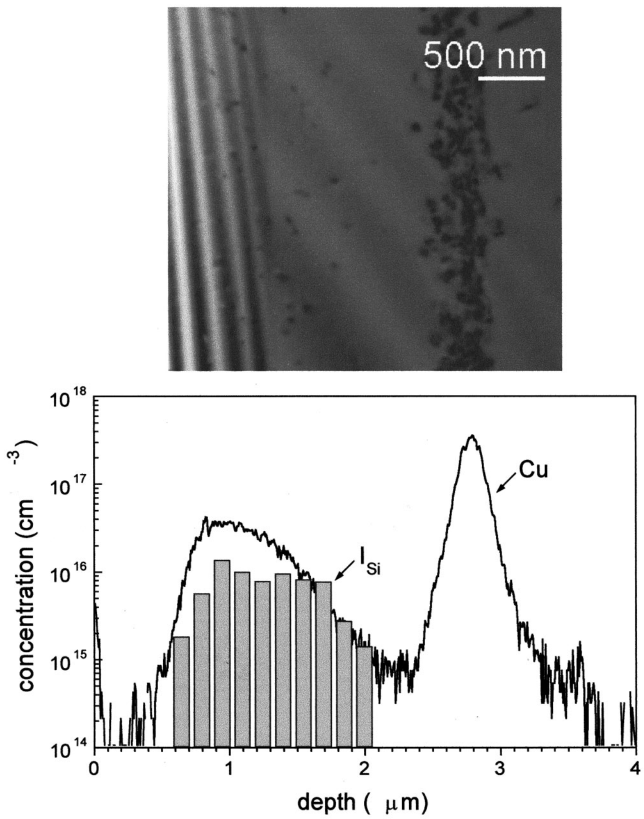

FIG. 2. Bright field XTEM micrograph (top) for self-ion-implanted FZ–Si (3.5 MeV, $5\times10^{15}\,\mathrm{Si}^+\,\mathrm{cm}^{-2}$) after annealing at 850 °C for 1 h. Loops of interstitial character are visible in the $R_P/2$ region. In the bottom part the associated Cu depth profile measured by SIMS is correlated with the concentration of Si atoms bound in loops (bars) that reflects the original interstitial stage.

We assume that self-interstitials are ejected during ion milling. Such an effect has been reported recently for sputter depth profiling of a SIMS specimen.[20] These preparation-induced interstitials may interact with self-interstitials or interstitial agglomerates which remain after MeV ion implantation and annealing to form larger (observable) interstitial loops. The loops are basically related to the original nucleation sites in the appropriate region. The concentration of Si atoms bound in loops at $R_P/2$ is shown in Fig. 2 by bars for each depth interval together with the Cu distribution. The defects visible in Fig. 2 around $R_P/2$ are not the gettering centers for Cu atoms because their appearance depends on the XTEM specimen preparation and their density is almost too low. However, the formation of interstitial loops can be taken as evidence for the supersaturation of self-interstitials or the existence of interstitial agglomerates in the $R_P/2$ region. Because of the presence of interstitial defects and the absence of vacancies we assume that the actual gettering centers for Cu atoms at $R_P/2$ consist of self-interstitial agglomerates which are too small to be directly visible in TEM. These interstitial agglomerates are nucleation sites for the formation of larger defects. It is noteworthy that the attributes of the gettering centers at $R_P/2$ are very similar to those of B-swirl defects which are known from previous investigations on crystal growth. They are assumed to be spherical agglomerates of self-interstitials in a liquid-like structure.[21] B-swirls form in Si at high temperatures and exist in a metastable state. During cooling down the B-swirls collapse to energetically more favorable A-swirls, which are interstitial-type loops. The B-swirls can be frozen in at room temperature as very small droplets if the transformation is inhibited, e.g., by the incorporation of carbon atoms which appear to stabilize B-swirls. The B-swirls are invisible by TEM and they can only be detected after decoration (gettering) with Li or Cu.[21,22] All these characteristics are close to those of the gettering centers at $R_P/2$.

The existence of interstitial-type defects in the gettering layer at $R_P/2$ after annealing at $T > 800\,°\mathrm{C}$ is in contradiction to the idea of a complete local recombination of all the created Frenkel pairs as proposed by the +1 model. Otherwise the temperature rise to a high temperature anneal would not leave nucleation sites at $R_P/2$ for the formation of interstitial defects. The +1 atoms are localized around R_P. The remaining point defects are mobile and can either outdiffuse toward the surface or agglomerate (or interact with impurities). An experimental result[23] shows the simultaneous supersaturation for both types of defects, vacancies and interstitials, around $R_P/2$ after annealing at 810 °C. The number of vacancies decreases with increasing annealing temperature (by about 80% for increasing temperature from 738 to 810 °C).[23] Simple point defects, like divacancies or vacancy–impurity pairs, disappear after annealing at 700 °C as has been shown by deep level transient spectroscopy (DLTS)[24] and electron paramagnetic resonance.[25] Interstitial agglomerates have been observed by DLTS after annealing at $T = 685\,°\mathrm{C}$ for fluences below the threshold for extended defect formation.[26]

A further argument for our suggestion that interstitial agglomerates are present in the $R_P/2$ region is the fact that Cu is trapped there. Two examples of gettering layers for Cu atoms are known, which clearly contain interstitial agglomerates caused by supersaturation of self-interstitials. One example concerns the silicon region beneath the SiO_2/Si interface of separated by implanted oxygen material,[27] and the other one—the crystalline layer close to an amorphous to crystalline interface.[28]

In summary, no vacancy-type defects have been detected by means of PAS in the $R_P/2$ region of MeV ion-implanted Si after annealing at 900 °C. Instead, interstitial loops have been found for XTEM specimens prepared under special conditions. These defects indicate that the $R_P/2$ defects are caused by small agglomerates of self-interstitials in the $R_P/2$ region.

The authors thank A. B. Danilin for performing the SIMS measurements and for valuable discussions.

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