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Gettering Centres for Metals and Oxygen Formed in MeV-Ion-Implanted and Annealed Silicon

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ABSTRACT

Damage occurs in MeV-ion-implanted Si not only at the projected ion range, R_P, but also around $R_P/2$ after annealing. A convenient way to detect this damage is to decorate it with metal atoms and to measure the metal distribution. Up to now no structural defects have been seen in the $R_P/2$ region. In this study the trapping of Cu atoms at $R_P/2$ is investigated in dependence on ion dose and energy. A high concentration of O impurities has been found to suppress the Cu gettering. No vacancy-like defects could be detected by positron annihilation spectroscopy after annealing at high temperatures of T>850°C. Instead, interstitial-type defects have been observed at $R_P/2$ using cross section transmission electron microscopy of specimen prepared under suitable conditions.

INRODUCTION

Ion implantation is a standard process for the precise and controlled introduction of dopants and other impurities into silicon crystals. However, the necessary annealing of the 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. Damage has been discovered after MeV ion implantation and annealing in the temperature range between 700 and 1000°C in two distinct depth regions, around the mean projected ion range, R_P, and also between the surface and R_P, mainly at $R_P/2$, by means of metal gettering [1-6]. The gettering efficiency of the defective layer at $R_P/2$ for metallic impurities is much higher than around R_P despite that no structural defects have been found in this region by cross section electron microscopy (XTEM) [3,6]. It is assumed that excess vacancies are the gettering centres which are generated in this region during ion implantation and may remain after annealing [3,5,7]. However, the origin of these gettering centres has not yet been proven. A better understanding of their detailed nature is necessary to avoid deterioration of electronic devices by trapping of undesired metallic impurities.

In the present study the trapping of Cu in the $R_P/2$ region of self-ion-implanted Si is systematically investigated for various ion doses and energies as well for different Cu contamination. Moreover, the interdependence of Cu and O impurity trapping is studied and the change is checked of the signal of variable energy positron annihilation spectrometry (PAS), an analysis method which is sensitive for vacancy-like defects.

EXPERIMENTAL

A gettering layer has been formed by implantation of Si^+ ions in the dose range of 1×10^{14} to 5×10^{15} cm^{-2} and in the energy range of 0.39 to 9MeV into (100)-oriented Cz-Si (4Ωcm) and Epi-Si (14Ωcm). The implantation damage has been annealed in Ar ambient either at 850°C for 30min or at 900°C for 30s. Cu has been subsequently introduced into the rear surface of the samples by ion implantation with 20keV to a dose of 3×10^{13} or 1×10^{15} Cu^+cm^{-2} and redistributed by a thermal treatment at 700°C for 3min. The Cu depth distribution has been determined by secondary ion mass spectrometry (SIMS). The presence of vacancy-like defects has been checked by PAS. Finally, the $R_P/2$ region has been analyzed by XTEM after specimen preparation using ion-milling in a „Gatan Duo Mill 600“ with 4keV Ar^+ ions under an incidence angle of 13°.

RESULTS and DISCUSSION

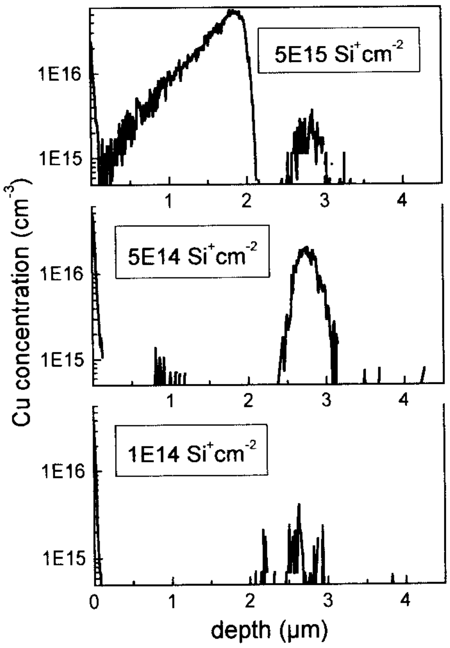

Fig.1
Cu depth profiles measured by SIMS for 3.5MeV (R_P=2.7µm) self-ion-implanted and annealed Si. Subsequently to annealing of 900°C, 30s Cu has been implanted into the rear side with 20keV to a dose of 3×10^{13} Cu^+cm^{-2} and redistributed throughout the sample by a thermal treatment of 700°C, 3min.

The Cu gettering at $R_P/2$ and at R_P is demonstrated in Fig.1 for Si^+-implanted Si to different doses. Obviously a higher ion dose is necessary to achieve a significant Cu gettering in the $R_P/2$ region. Below a threshold dose gettering by the damaged layer at R_P is dominating. Above the threshold dose gettering at $R_P/2$ is clearly stronger. The difference of binding energies of Cu has been determined to be $\Delta E_{Cu}=E(R_P/2)-E(R_P)=1.35$eV [4]. The change of gettering efficiency at the threshold dose probably corresponds to a change of the defect structure of $R_P/2$ -and/or R_P region. For the $R_P/2$ region no information is available about any defect structure. For the R_P region the threshold dose approximately corresponds to that ion dose for which extended secondary defects (dislocation loops) are formed during annealing. The condensation of implantation-induced self-interstitials at dislocation loops seems to reduce the gettering efficiency of the R_P region for Cu.
An increase of the Cu contamination level results in a trapping of additionally introduced Cu at R_P (not shown) in spite of the higher binding energy to the gettering layer at $R_P/2$. This is caused by the rapid cooling in our experiment. Cu gettering is a diffusion-limited process and takes place in the temperature range between 500 and 700°C [4]. At temperatures T>800°C Cu is dissolved throughout the whole bulk-material. Therefore, the R_P layer is located closer to the source of Cu and accumulates more Cu during quenching. Either slow cooling or post-annealing at temperatures between 500 and 700°C for several minutes is necessary to reach the equilibrium occupation of Cu for the two gettering layers [4]. However, the total number of gettering sites at $R_P/2$ seems to be limited as the maximum Cu concentration never exceeds 10^{18} cm^{-3}.

The variation of the Si^+ ion energy results in a significant shift of the gettering layer at $R_P/2$ with respect to the R_P layer. This is shown in Fig. 2. The R_P part of the Cu depth profiles is cut to have a figure easy to survey. As the Si^+ ion dose is constant for all implants the amorphization threshold has been exceeded during implantation for the two lower energies. The shape of Cu depth profiles at $R_P/2$ is more flat for lower energies and its maximum shifts to R_P for higher energies.

However, the term "$R_P/2$ effect" used in the literature [6] is not misleading as the maximum Cu concentration is close to $R_P/2$ for the frequently used MeV energy range of 0.5 to 5MeV.

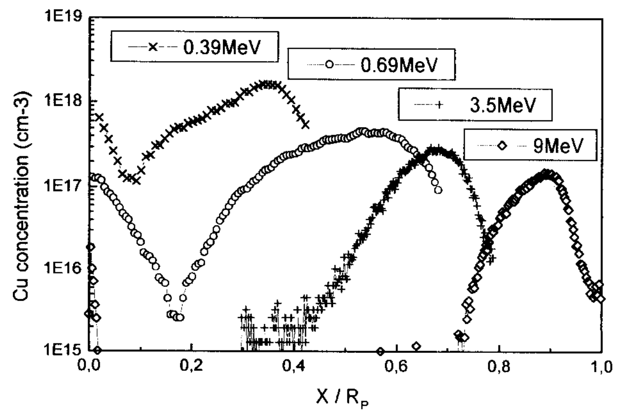

Fig. 2
Cu depth profiles of the $R_P/2$ region for self-ion-implanted Cz-Si (dose: 5×10^{15} Si^+cm^{-2}) after annealing of 950°C, 30s.
Cu was subsequently introduced into the rear side and diffused throughout the bulk by thermal treatment of 700°C, 3min.
The depth scale is normalized to R_P to make comparable the different Cu depth profiles.

The origin of the gettering centres at $R_P/2$ can be discussed in terms of the excess vacancy model [7]. It is assumed that the gettering sites are excess vacancies which are generated during ion implantation and remain after the complete local recombination of implantation-induced intrinsic point defects.

The Cu profiles at $R_P/2$, as shown in Fig. 2, agree well with calculations on excess vacancies generated by ion implantation [7]. However, the total concentration of Cu in the $R_P/2$ region is only 1% of the predicted excess vacancy concentration which amounts to about 0.01% of the displacements of Si lattice atoms generated by ion implantation [3,7]. It has to be taken into account that it is the as-implanted excess vacancy concentration. During annealing these point defects may diffuse toward the surface or to the R_P region where they can recombine. A very rough estimation of such a diffusion process can be done using our data reported in Ref. 6. Our simple assumption made for the disappearance of the $R_P/2$ effect is that the diffusion length of point defects ($L=\sqrt{(D\times t)}$) should be at least half the distance between surface and R_P. This distance is about 1μm (see Fig. 1). The diffusivity of point defects ($D_{I,V}$) is adopted of the TEchnology SIMulator (TESIM). More detailed calculations have been published in Ref. 7.

Tab. 1: Occurrence of the $R_P/2$ effect for 3.5MeV, 5×10^{15} Si^+cm^{-2} > Si [6]

950°C, 30s	$R_P/2$ effect: Yes	$L=\sqrt{(D\times t)}$= 0.55μm
950°C, 2min	$R_P/2$ effect: No	$L=\sqrt{(D\times t)}$= 1.10μm

The result of Tab. 1 is also in fair agreement with the excess vacancy model. The problem of the excess vacancy model is that vacancy defects acting as gettering centres after annealing at temperatures T>800°C have not yet been proven. This subject is discussed below.

Besides metal impurities also O impurities can be trapped at the two gettering layers. Such an O trapping has been reported after annealing at high temperature of 1000°C [8]. Moreover, in a vacancy rich region ($R_P/2$) the O precipitation proceeds already at temperatures as low as 400°C and the vacancies are consumed by O precipitation [9]. In Cz-Si an as-grown O concentration of about 1×10^{18} cm^{-3} is always present. Therefore, the interdependency of Cu and O gettering at $R_P/2$ has been checked by an additional implantation of O into Epi-Si of a low O impurity content of 1.2×10^{16} cm^{-3}.

The Cu depth profiles in Fig. 3 show that an additional gettering layer occurs beside the $R_P/2$ and R_P region at the Epi/Cz interface. The O-implanted region located at a depth of about 1.5μm obviously does not trap Cu whereas the region containing few O acts as a gettering centre. The maximum O concentration of 2×10^{19} cm^{-3} is by a factor of 10 higher than in CZ-Si. This means that for annealing in the used temperature range of 800 to 950°C the presence of an enhanced O concentration suppresses the Cu gettering. The inverse conclusion is that the occurrence of Cu gettering at $R_P/2$ in Cz-Si indicates the absence of O impurity trapping or precipitation. Otherwise the high O concentration would consume the available gettering sites.

O trapping and precipitation in the $R_P/2$ region is a competitive process to Cu gettering. Because of the low mobility of O in Si its trapping can only take place either for concentrations significantly exceeding the amount contained in Cz-Si (1×10^{18} cm^{-3}) or for stronger anneals. Similar results have been reported for experiments to study the behavior of O impurities in ion implanted Cz-Si [2].

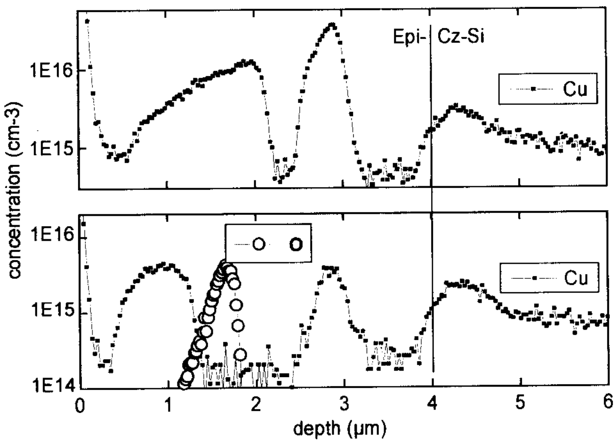

Fig. 3
SIMS depth profiles in Epi-Si for implantation with 3.5MeV Si^+ ions to 5×10^{15} Si^+cm^{-2} and annealing at 850°C for 30min. Cu was introduced into the rear and redistributed by a thermal treatment of 700°C, 3min.
The bottom figure shows the TRIM result for an additional implantation of 1.4MeV O^+ ions to 5×10^{14} O^+cm^{-2}.
The O depth profile is scaled down by a factor of 2×10^{-4}. The maximum O concentration is about 2×10^{19} cm^{-3}.

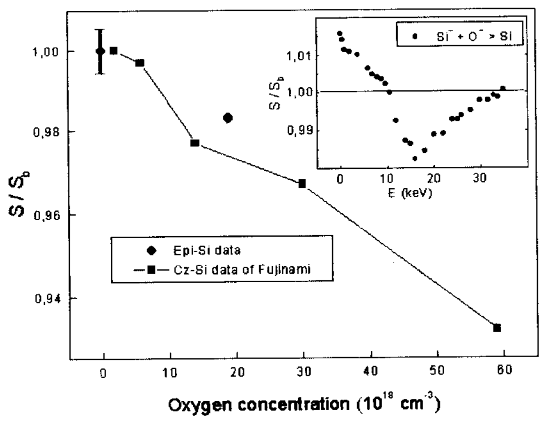

Fig. 4
Normalized S-parameters of Epi-Si and Cz-Si after O^+ ion implantation and annealing versus the maximum O concentration.
Epi-Si data correspond to the samples as shown in Fig. 3.
Cz-Si data are taken of Ref. 11.
S/S_b decreases linearly as the O concentration increases.

PAS has been used to check for vacancy defects in the $R_P/2$ region of MeV-ion-implanted Si. The results show that vacancy-like defects are present for the as-implanted sample as the normalized S-parameter is $S/S_b>1$. The dominant vacancy-like defects are divacancies (*VV*). This is indicated by their value $S/S_b=1.037$. Because of the saturation of positron trapping the total *VV* concentration is $c_{VV} > 10^{18}$ cm^{-3}. After a thermal treatment at high temperatures T>850°C in each case (with and without Cu contamination) the vacancy defects disappear, as $S/S_b<1$. This result has been found also for samples for which the $R_P/2$ effect is clearly seen and it is in general agreement with other investigations [3]. This means that the vacancy-like defect concentration decreases during thermal treatment at T>850°C below the PAS detection limit of about 1×10^{15} cm^{-3} [10]. This value is about two orders of magnitude lower than the maximum concentration of Cu gettered at $R_P/2$.

On the other hand, O precipitates possibly formed during annealing at 850°C in a vacancy-rich region decrease the S/S_b value [11]. The S-parameter for SiO_2 is known to be lower than for bulk-Si. We analyzed our Epi-Si samples by PAS after performing a HF dip to remove the native surface oxide. The measured S/S_b values are shown by the insert in Fig. 4 as a function of positron energy (E) for the sample with the additional O implantation. The minimum of S/S_b corresponds to the maximum concentration of O. The data in Fig. 4 demonstrate that S/S_b linearly decreases as the O concentration increases. However, the change of S/S_b by a small O concentration of 1×10^{18} cm^{-3}, as for Cz-Si, is inside the error limits of the experiment. O impurities in Cz-Si cannot change the PAS results without significant O accumulation. For thermal treatments used in this study an accumulation of O impurities is not observed [2]. The final result is that no vacancy-like defects at $R_P/2$ have been detected by PAS.

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 with a size of about 20nm. Their interstitial character has been analyzed by diffraction contrast. Density and depth distribution of the loops correlate well 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.

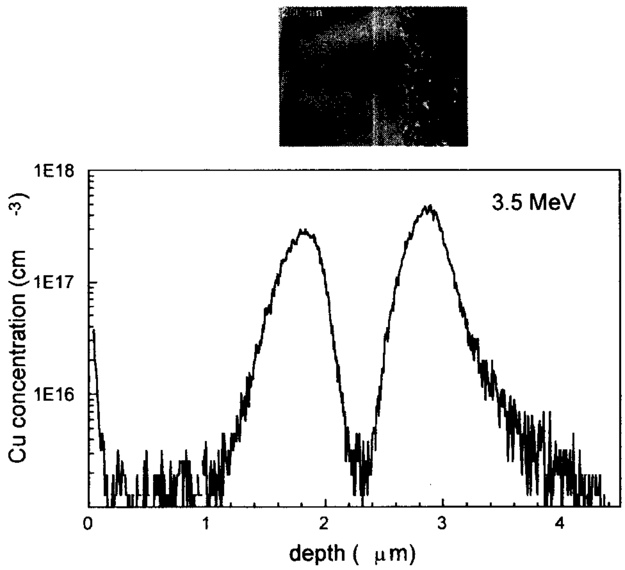

Fig. 5
Bright field XTEM micrograph (top) for Cz-Si implanted with 3.5MeV Si^+ ions to 5×10^{15} Si^+cm^{-2} after annealing of 950°C for 30s. Small loops of interstitial character are visible in the $R_P/2$ region.
In the bottom figure the associated Cu depth profile measured by SIMS is shown in the same depth scale.

One example is presented in Fig. 5 (top) and compared with the corresponding Cu depth profile (bottom). The defects have been found after thinning the XTEM specimens by ion-milling under special conditions.

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^o. More details are published in Ref. 12. This result can be explained by assuming that self-interstitials are ejected during ion-milling. These preparation-induced interstitials interact with self-interstitials which remain after MeV ion implantation and annealing to form larger (observable) interstitial loops. The loop density is probably related to the original interstitial supersaturation. The defects visible in Fig. 5 around $R_P/2$ are *not* the gettering centres 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 in the $R_P/2$ region. Because of the supersaturation of self-interstitials and the absence of vacancies we suggest the actual gettering centres for Cu atoms at $R_P/2$ to consist of self-interstitial agglomerates which are too small to be visible in TEM.

SUMMARY

Cu and O atoms are gettered in MeV-ion-implanted and annealed Si in two regions of different damage structure. The gettering at $R_P/2$ is usually explained by excess vacancies. Their predicted formation during ion implantation and their diffusion-limited recombination during annealing can describe the appearance and disappearance of the $R_P/2$ effect. However, these defects have not yet been proven. 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 $T>850^oC$. Instead, interstitial loops have been found for XTEM specimens prepared under suitable conditions. This can be taken as evidence for a supersaturation of self-interstitials in the $R_P/2$ region. The results obtained encourage us to suggest another interpretation in that the gettering centres at $R_P/2$ are agglomerates of self-interstitials.

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