Direct observation of voids in the vacancy excess region of ion bombarded silicon

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The results reported in this letter indicate that the spatial separation of the vacancy and interstitial excesses which result from ion bombardment gives rise to stable voids upon annealing at 850 °C even for implants where the projected ion range is only of the order of a few thousand Ångstrom. Such voids have been observed directly by transmission electron microscopy. Furthermore, in cases where both voids and interstitial-based defects are present at different depths, it is found that Au has a strong preference for decorating void surfaces and hence Au can, indeed, be used as a selective detector of open volume defects in Si. © *2001 American Institute of Physics.*
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Ballistic processes which occur during implantation into Si lead directly to a local vacancy excess at depths up to about half the projected ion range and an interstitial excess at deeper depths close to the ion range.[1] However, there is considerable interest as to the stability of such defects and their evolution during annealing.[2–5] Whereas interstitial-based {311} defects and loops[2–4] are easily observed by transmission electron microscopy (TEM), vacancy clusters and voids have been extremely difficult to observe directly.[5] Nevertheless, voids have been observed by TEM after annealing of MeV implants to high doses,[6,7] where the separation of the vacancy and interstitial excesses is large, and also inferred[8] from contrast in TEM images following high dose keV implants. However, as a result of this difficulty of observing voids, indirect methods have been used to determine vacancy excesses such as positron annihilation[9] and also labelling of vacancy clusters by fast diffusing metals,[5,10,11] such as Au. Positron annihilation is sensitive to open volume defects but the vacancy concentration needs to be high ($\sim 4\times10^{16}$ cm^{-2}).[12]

It is well known that fast diffusing metals are efficiently trapped at nanocavities in silicon[13,14] and these larger open volume defects are easily observable by TEM. However, there is some debate as to whether metals are selectively gettered to vacancy clusters in the presence of interstitial-based defects. Some authors[15] suggest, for example, that metal decoration at defects which are not observable by TEM at around half the projected range ($R_p/2$) may not be proof that stable vacancy clusters exist in this region. However, the recent Au decoration studies of so called $R_p/2$ defects for MeV implants[10,11] is quite convincing in arguing for the presence of vacancy clusters.

In this study we set out to directly observe vacancy-related defects in TEM for keV implantations and to attempt to resolve the issue of open volume defects being preferential trapping sites for fast diffusing Au.

Czochralski (Cz) Si (100) wafers (*n*-type 5–10 Ω cm) were implanted with 245 keV Si^+ ions at 100 °C to doses in the range 8×10^{14}–6×10^{16} cm^{-2}. The base pressure during implantation was better than 10^{-7} Torr. The projected ion range R_p for 245 keV Si^+ ions in Si is 3800 Å, as obtained from TRIM95 simulations.[16] Such simulations were also used to provide the excess vacancy and interstitial distributions, as shown in Fig. 1. It is clear that collisional processes lead to an excess of vacancies from the surface up to a depth of about $R_p/2$, whereas the interstitial excess (which includes the implanted ions themselves) is located at depths close to R_p. Following implantation, samples were annealed at 850 °C for 1 h to allow defect annihilation and/or clustering into defects visible by TEM. Selected samples had a 5×10^{13} cm^{-2} Au implant at 30 keV prior to annealing (R_p<200 Å) to allow Au decoration of defects during subsequent annealing at 850 °C. Samples were analyzed before and after annealing by Rutherford backscattering and channeling (RBSC) using 1.8 MeV He^+ ions to monitor implantation damage and Au distributions. Selected samples were analyzed by cross-sectional TEM (XTEM) using a CM 300 instrument operated at 200 keV in order to study the nature of residual defects.

Figure 2 shows RBS profiles of Au for two Si^+ doses, 3×10^{15} cm^{-2} and 1.4×10^{16} cm^{-2}, after annealing at 850 °C. For the lower Si^+ dose case, about 35% of the Au is located in a broad peak centred at about 900 Å. The remainder of the Au remains at the surface, presumably where it has precipitated. Based on the recent report of Kalyanaraman *et al.*[11] this result would suggest that Au has completely filled the residual open volume defects in the sample. Using their calculated value of 1.2 vacancies per Au atom, this would give the number of vacancies bound up in such clusters as 3×10^{13} cm^{-2} for a dose of 3×10^{15} Si cm^{-2} at 100 °C. The higher Si^+ dose case in Fig. 2 shows that almost all the Au has distributed to depths between the surface and $R_p/2$. This result would suggest that there is insufficient Au to saturate the open volume defects. It is interesting that there is a double peak in the Au profile in this case (see second peak at 2400 Å), a feature we will return to later. In addition, there is a zone near the surface (<200 Å) which is denuded of any Au. This region corresponds to a surface

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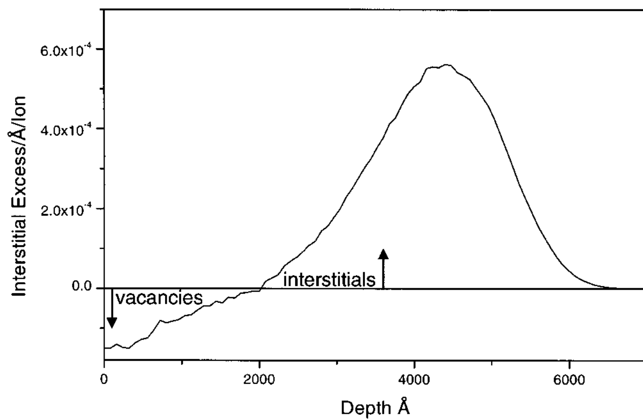

FIG. 1. TRIM simulations using full cascades, illustrating the vacancy and interstitial excesses as a function of depth for 245 keV Si ions incident on a Si sample. The incident ions are included in the interstitial excess.

layer which has been amorphized by the Au implant. Amorphization would be expected to destroy any residual defects emanating from the prior 245 keV Si^+ implant.

In Fig. 3(a), we show a cross-sectional TEM micrograph corresponding to the higher dose case in Fig. 2. Considerable residual disorder follows the 850 °C annealing in this case. However, the visible defects are essentially all interstitial-based dislocation loops and tangles. Comparing the depth distribution of this visible damage with the corresponding Au distribution from Fig. 2, it is clear that most of the Au lies at depths where no visible dislocations are present. In Fig. 3(b) we show RBSC spectra illustrating the residual disorder before and after annealing. Before annealing, the disorder peak in RBSC just reaches the random level but is not completely amorphous at this dose, suggested by the nature of the residual defects observed in the XTEM after annealing [Fig. 3(a)]. The RBSC spectrum after annealing shows a little residual disorder beginning at about 3500 Å, illustrating the low sensitivity of RBSC to moderate concentrations of extended defects.

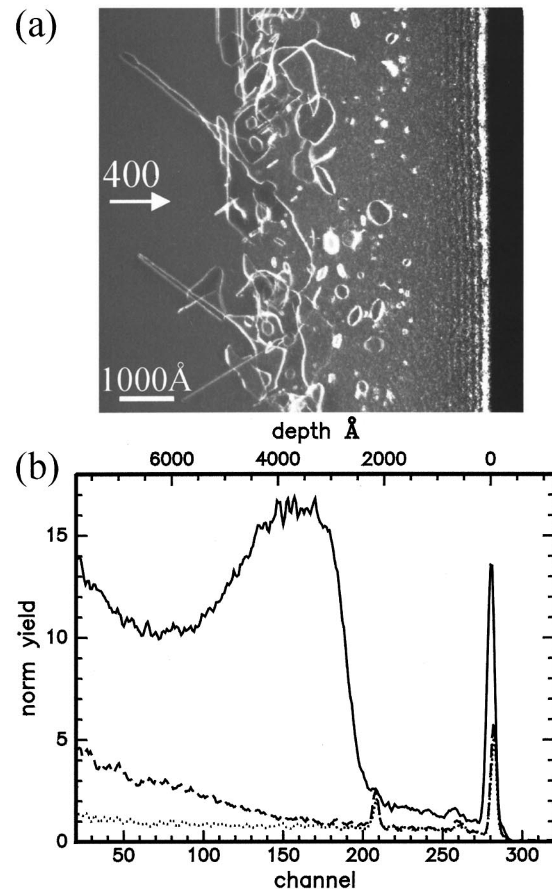

FIG. 3. (a) XTEM micrograph of the 1.4×10^{16} cm^{-2} sample from Fig. 2. (b) RBSC spectra of this same sample before (solid curve) and after (dashed curve) annealing at 850 °C. The dotted curve depicts a spectrum from an unimplanted sample.

In order to determine what defects are decorated by the Au, higher magnification XTEM was examined. Figure 4 shows such a TEM micrograph for the 1.4×10^{16} $Si\,cm^{-2}$ dose after annealing, clearly showing the presence of voids. The top of the micrograph is about 460 Å from the surface of

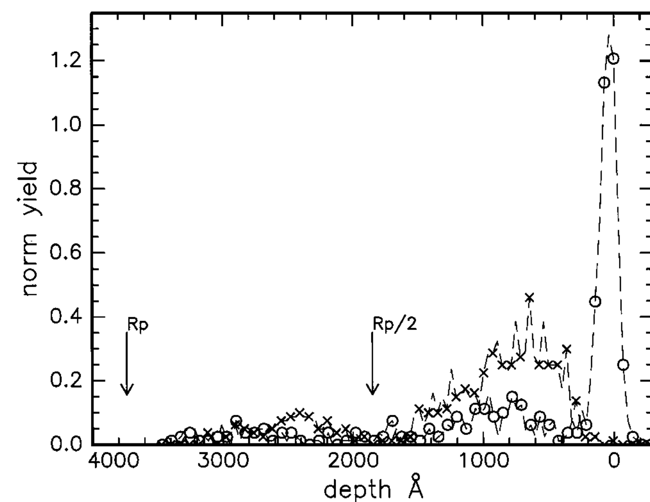

FIG. 2. RBS spectra of Au profiles after annealing at 850 °C for 1 hr of Si samples previously implanted with 245 keV Si^+ ions at 100 °C to doses of 3×10^{15} cm^{-2} (open circles) and 1.4×10^{16} cm^{-2} (×). After Si implantation a 30 keV Au implant to a dose of 5×10^{13} cm^{-2} was carried out at room temperature.

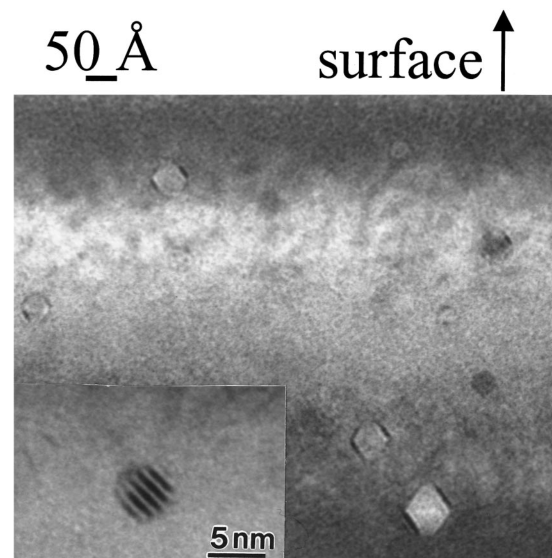

FIG. 4. XTEM micrograph from a depth (460–1100 Å from the surface) corresponding to the region denuded of interstitial-based defects but containing Au for the 1.4×10^{16} cm^{-2} sample from Fig. 2. The inset shows a precipitate which is presumably Au rich.

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the sample, whereas the bottom of the micrograph corresponds to a depth of about 1100 Å from the surface. This region has been shown to be devoid of visible defects in the lower magnification micrograph in Fig. 3(a). Figure 4 is taken slightly out of focus to improve imaging of voids. The voids are well faceted and about 50 Å in size. Through-focal imaging of the voids showed Z-contrast arising from the Au decoration of the walls of the voids as has been previously observed for the case of Au gettering to much larger nanocavities.[13]

XTEM analysis of the sample also revealed the presence of occasional precipitates which have a similar size to the voids. These precipitates sometimes exhibit well defined Moiré fringes (see inset), which are indicative of a crystalline phase with a different lattice spacing to that of the Si matrix, presumably an Au rich phase. We propose that, as has been well established for nanocavities in Si,[17] when the Au concentration exceeds that required to saturate the void walls at around a monolayer of coverage, it then begins to fill the open volume of the voids. It would appear that when all the open volume is filled by Au, the excess Au prefers to precipitate at the surface rather than decorate interstitial-based defects. Our observations for lower and higher Si^+ doses than the 1.4×10^{16} cm^{-2} case, illustrated in Figs. 2, 3, and 4, are consistent with this behavior.

Voids have only previously been observed at depths less than the projected range for oxygen[6,7] and phosphorous[8] implanted Si. This raises the question as to whether impurities or a chemical effect might be responsible for stabilizing voids during annealing. In our case of Si^+ implantation, such an impurity or chemical effect could only arise from background impurities in the Si itself (such as oxygen in Cz Si) or from recoil implanted oxygen.[18] Based on the low partial pressure of oxygen under our implantation conditions, we believe we can rule out any role of recoiled oxygen. In the case of background oxygen (or carbon) in the Si itself, there may be some role in the initial trapping of vacancies but it is unlikely that such impurities play a major role in their subsequent coalescence into voids. For example, annealing temperatures of 950 °C for several hours are required to redistribute oxygen to nanocavities in Si,[19] whereby oxygen ejects Au from cavity walls.

The deeper Au peak in Fig. 2, at about 2400 Å for the 1.4×10^{16} Si cm^{-2} case, deserves some discussion. From Fig. 3(a), this Au resides in the edge of the region containing dislocations. However, detailed examination by TEM also showed a band of faceted voids at precisely this depth. These voids were larger than the voids in the shallower band. We suggest that Au is selectively decorating voids at this depth rather than loops. The fact that there is a deficiency of Au at depths between about 1500 and 2000 Å and that this also corresponds to a region devoid of voids is intriguing. It appears that, at depths close to the boundary between vacancy and interstitial excesses, both voids and loops may coexist. The voids may be significantly larger because of the presence of loops which absorb the interstitials. Furthermore, this behavior may be more pronounced in our case compared with MeV implantation as a result of the close spatial proximity of vacancy and interstitial excesses. Whether point defects coalesce or annihilate may depend on their concentration, the dose rate, and irradiation temperature. In the region denuded of voids (and Au decoration), this fine balance may have resulted in annihilation rather than coalescence into voids and interstitial clusters.

Finally, the observed Si^+ dose dependence of void formation as monitored by Au decoration leads to some interesting conclusions. For doses below about 3×10^{15} cm^{-2} there is essentially no Au decoration of $R_p/2$ defects, suggesting that the vacancy excess may be too dilute to form stable vacancy clusters and voids, or alternatively, such clusters do not survive annealing. The results for the 3 and 8×10^{15} cm^{-2} Si^+ doses indicate that the number of excess vacancies per ion that contribute to stable voids on annealing is extremely low (~0.01). This number for 245 keV Si^+ ions at 100 °C is lower than that for 2 MeV Si at 70–80 °C (~0.04) as obtained by Kalyanaraman *et al.*[11]

In conclusion, we have shown direct evidence for the formation of stable voids at $\leqslant R_p/2$ for 245 keV Si^+ irradiation of Si at 100 °C, followed by annealing at 850 °C. Furthermore, Au has a strong preference for decoration of voids rather than interstitial-based defects, indicating that Au is an excellent selective detector for open volume defects.

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