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Selectivity of nanocavities and dislocations for gettering of Cu and Fe in silicon

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The selectivity of interstitial-based extended defects (loops) and nanocavities for the gettering of Cu and Fe in Si has been studied. Controlled amounts of Cu and Fe were introduced by ion implantation into wafers containing pre-existing nanocavities and/or dislocations. Results show that Cu has a strong preference for gettering to open volume defects, even when high concentrations of interstitial-based loops are present in close proximity. However, the gettering of Fe in samples containing both vacancy- and interstitial-type defects is more complex, with Fe accumulation at all regions in the sample which contain defects, whether they are vacancy- or interstitial-like in character. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1363689]

The use of ion-implantation-induced defects as efficient gettering sites for metal impurities in Si has generated much recent interest.[1–9] For example, the so-called end-of-range defects at the projected ion range, R_p, which evolve into well defined interstitial-based dislocation loops upon annealing, are found to be favorable sites for the accumulation of metals such as Cu[1,4] and Fe.[4,5] Recently, it has been observed[10–13] that metals can accumulate at depths close to $R_p/2$, and residual open volume defects (vacancy clusters and voids) have been suggested as the reason for this behavior.[10,11] Indeed, Brown *et al.*[13] indicated that Cu, Fe, and Ni could be gettered to residual defects from MeV Si$^+$ ion implantation at either R_p or $R_p/2$ (or both) depending upon the annealing conditions. Furthermore, it has been shown that Au accumulates preferentially at $R_p/2$ defects (most likely voids) generated by both MeV[10] and keV[14] Si ion bombardment. However, other studies[12] of Cu gettering to $R_p/2$ have questioned the interpretation of gettering to voids and suggested that Cu may be accumulating at interstitial-based defects close to $R_p/2$. In an attempt to clarify the selectivity of open volume defects or interstitial-based defects as gettering sites for certain metals, in this study we have investigated gettering of Cu and Fe to both nanocavities and interstitial-based loops.

It has previously been shown that metals such as Cu,[7–9,15] Au,[3] and Fe[6] can be trapped at strong bonding sites on cavity walls. Furthermore, it has been shown that Au is more strongly gettered to cavities than dislocation loops.[3] For Cu, both dislocations[5] and cavities[7–9,15] appear to be suitable gettering sites, but there have been no studies to determine preferred sites when defects of both types are present. The trapping and precipitation of Fe at defects in Si appears to be quite complex: Fe can precipitate at the surface, at Si–SiO$_2$ interfaces,[16] and in regions containing dislocations,[13] as well as induce defects in Si, such as stacking faults.[17] Again, no previous studies have directly compared the gettering of Fe to both open volume and interstitial-based defects in the same sample. Results from the current study clearly show that Cu strongly prefers open volume defects as gettering sites whereas the trapping and precipitation processes for Fe are considerably more complex.

Cz Si wafers (5–10 Ω cm, *n*-type) were separated into four batches, and samples from each batch were implanted and annealed according to the sequence in Table I. To form cavities, samples from batches 2 and 4 were first implanted with 40 keV, 3×10^{16} H cm^{-2} at room temperature and then annealed (in flowing Ar gas) at 850 °C for 1 h. This generated a band of nanocavities centred at a depth of ~4000 Å. A 140 keV Si$^-$ implant was then carried out at 250 °C to a dose of 1×10^{16} cm^{-2} into samples from batches 3 and 4. These samples were subsequently annealed at 850 °C for 1 h to form a band of extrinsic (interstitial-based) dislocation loops centred at about 2000 Å. Samples from all batches were then implanted with either Fe or Cu at 35 keV to a dose of 5×10^{13} cm^{-2} at room temperature followed by annealing at 850 °C for 1 h. All samples were analyzed by secondary ion mass spectrometry (SIMS) using a Riber MIQ256 apparatus with 8 keV O$_2^+$ ions to provide concentration versus depth profiles of Fe and Cu. Selected samples were analyzed by cross-sectional transmission electron microscopy (XTEM) in a Philips 430 electron microscope to monitor the distribution of residual defects.

Directly after implantation, the SIMS profiles of Fe and Cu were similar to those expected from TRIM95 simulations,[18] with projected ion ranges of around 300 Å. When samples implanted only with metals are annealed at 850 °C, almost all of the metals are redistributed within the

TABLE I. Implantation and annealing sequence for various sample batches.

Sample batch	H implant	Anneal 850 °C	Si implant	Anneal 850 °C	(Fe, Cu) implant	Anneal 850 °C
1	No	No	No	No	Yes	Yes
2	Yes	Yes	No	No	Yes	Yes
3	No	No	Yes	Yes	Yes	Yes
4	Yes	Yes	Yes	Yes	Yes	Yes

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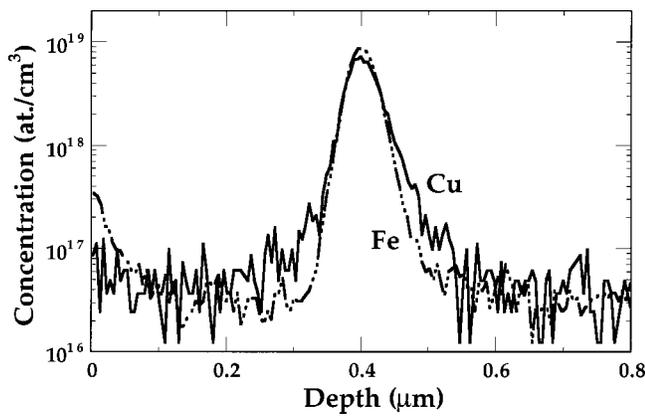[b]Electronic mail: jsw109@rsphysse.anu.edu.au

FIG. 1. SIMS concentration versus depth profiles for Cu (solid curve) and Fe (dashed curve) following annealing at 850 °C for 1 h of samples containing a band of cavities at a depth of around 4000 Å.

FIG. 3. XTEM image (a) and SIMS Fe concentration versus depth profile (b) for a sample containing both interstitial-based loops and cavities following annealing at 850 °C for 1 h.

initial implanted layer, presumably trapped at the surface or within implantation-induced defects.[9,15] For samples containing only nanocavities, i.e., batch 2, essentially all of the Cu and Fe was relocated during annealing to the cavity band. This is illustrated in Fig. 1, which shows that the annealing conditions of 850 °C for 1 h are sufficient to fully release both metals from trapping sites within the implanted layer and permit complete diffusion to the cavity band. It has previously been shown that both Cu[7–9,15] and Fe[6] have a strong affinity for bonding to cavity walls. In the case of batch 3, where only disorder from the Si ion implantation was present, the Cu and Fe were found to exhibit differences. For example, essentially all the Cu was relocated to the region where the dislocation band was expected, whereas most of the Fe was located within the first few hundred angstroms from the surface, with only a small fraction decorating the

dislocation band, as presented in more detail elsewhere.[19]

The behavior of Cu and Fe in samples containing both dislocations and cavities is illustrated in Figs. 2 and 3, respectively. For Cu, Fig. 2(a) shows a band of dislocations centered at about 2000 Å, and the nanocavities at around 4000 Å. There is little visible disorder in Fig. 2(a) in the near-surface region, both where the original Cu implant was located and up to a depth of about 1000 Å. However, higher magnification TEM micrographs under appropriate imaging conditions did reveal the presence of voids from the surface up to about 1000 Å. Such a void distribution corresponds to the vacancy excess region ($R_p/2$ defects) arising from the Si implantation. In Fig. 2(b) we show the corresponding SIMS Cu profile plotted on the same depth scale. It is clear that essentially all of the Cu has selectively decorated the cavities, although a high concentration of extrinsic loops is present in this sample as well. The 5×10^{13} Cu cm^{-2} dose will give less than a monolayer coverage of the cavity walls under the H-implant and anneal conditions used in this study.[15] We anticipate that the void concentration for a 1×10^{16} Si cm^{-2} dose may be too low to result in a significant amount of Cu decorating the walls of these defects in comparison with the much larger surface area of the cavities.[20] Overall, the results for Cu show that, in the absence of cavities or a sufficiently high void concentration, Cu will decorate dislocations. However, if both interstitial-based defects (dislocations) and open volume defects (nanocavities) are present in the same sample, Cu strongly prefers to decorate
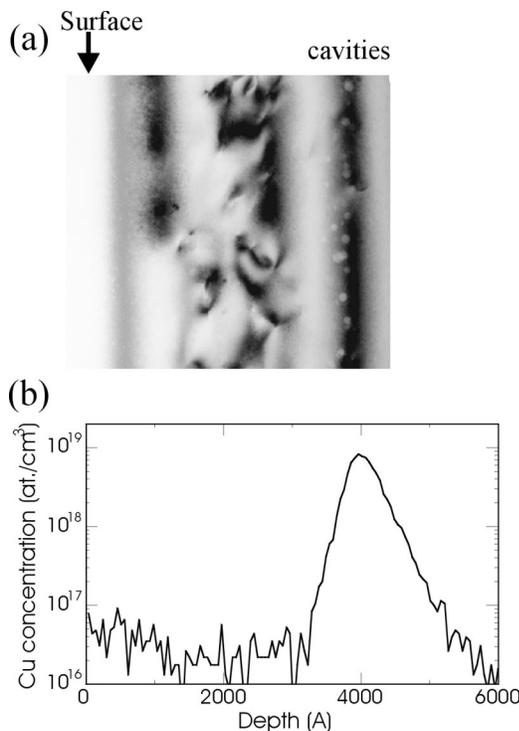

FIG. 2. XTEM image (a) and SIMS Cu concentration versus depth profile (b) for a sample containing both interstitial-based loops and cavities following annealing at 850 °C for 1 h.
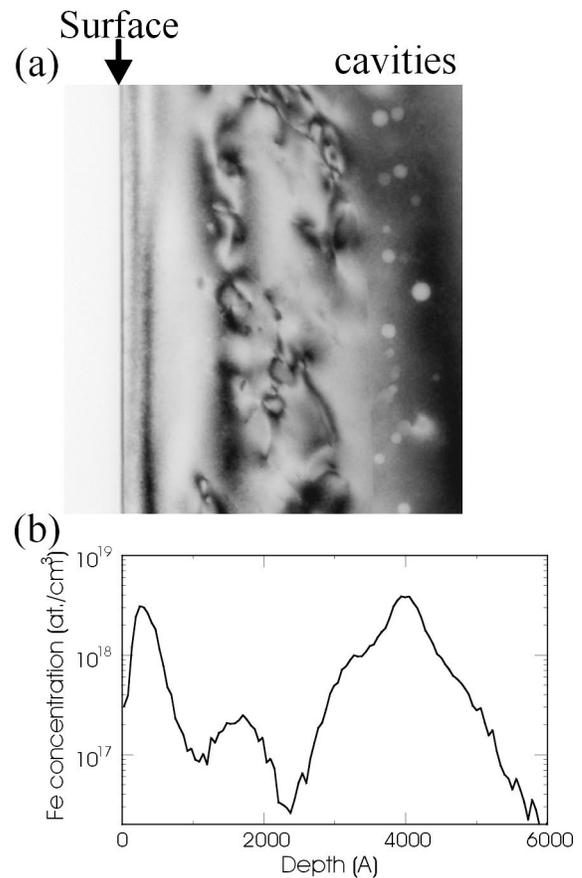
open volume defects under the annealing conditions of this study.

These Cu results impact on the work by Kögler *et al.*,[12] who observed Cu gettering to defects at half the projected range ($R_p/2$) for MeV Si implants and have suggested that Cu may be preferentially gettered to observed interstitial-based defects. However, other studies have established that excess vacancies at $R_p/2$ coalesce into voids on annealing.[14,21,22] In light of this controversy, our results indicate that, even if both interstitial-based and open volume defects coexist at $R_p/2$, the Cu would have a strong preference for decorating cavity or void walls.

When both dislocations and nanocavities are present in the same sample, the SIMS profile in Fig. 3(b) clearly shows that Fe decorates several defective regions. A considerable fraction of Fe remains trapped in its own implanted region within 500 Å of the surface. It is not possible to establish, from the corresponding XTEM micrograph in Fig. 3(a), the nature of the defects at which Fe is located. However, it has previously been shown that Fe can precipitate at a surface oxide[16] and induce stacking faults within the near surface region[17] at which it precipitates. The second peak in the Fe distribution at about 1800 Å corresponds to a high density of extrinsic dislocations in the front half of the dislocation band [Fig. 3(a)]. Indeed, the first two Fe peaks in Fig. 3(b) are qualitatively similar to those in a sample only containing residual disorder from the Si implant (batch 3). In addition, the highest fraction of Fe resides at the cavity band depth centered at 4000 Å. Finally, compared with the Cu distribution in Fig. 2(b), the Fe distribution is quite broad, suggesting that it also decorates dislocations surrounding cavities.

In contrast to the Cu behavior, where the SIMS profiles correspond closely with the defect distributions as obtained from XTEM, the Fe behavior is quite complex. The Fe distribution does not mirror the observable defect distributions: a considerable fraction of the Fe, particularly in the near-surface region, cannot be correlated with defects visible in XTEM. For example, some of the Fe may have precipitated at the native oxide interface, stacking faults, residual disorder from the Fe implant, or voids from the Si implant. However, the density of such Fe precipitates may be too low to be easily observable by TEM in the presence of more abundant loops and cavities. Nevertheless, it was possible to observe precipitates at the surface of samples with only the Si implant, although these could not be unequivocally identified with an Fe phase. Furthermore, there is evidence, from the difference between Fe profiles from the various sample batches, that there may be considerable interaction between the various defect profiles (in batch 4) during annealing. For instance, when only cavities are present, essentially all the Fe is gettered to them on annealing but if dislocations and cavities are both present, a considerable fraction of the Fe is gettered to neither of these defect bands and prefers to reside close to the surface. This possibility of defect interactions, which add to the complex gettering behavior of Fe, warrants further study.

Care needs to be exercised before the specific observations in this study are generalized. It has previously been shown that very low area densities of Cu($\leqslant 5\times10^{10}$ cm^{-2}) introduced by contamination are also extremely efficiently

gettered to open volume defects.[23] In addition, Cu appears to selectively trap at open volume defects in Si over a range of annealing conditions (from 650 to 950 °C).[15,19,23] Thus, it does appear that Cu prefers to decorate open volume defects over a range of experimental conditions regardless of how Cu is introduced into the Si. There have not been such extensive comparisons made for Fe, but from both the current study and previous studies reviewed in Ref. 9, it is clear that many factors, such as how Fe is introduced into Si, the manner in which defects are introduced, and annealing conditions, influence trapping and precipitation processes of Fe in Si.

In conclusion, under the experimental conditions of this study, we have shown that Cu strongly prefers open volume defects as gettering sites in Si. If, however, there are insufficient open volume defects to accommodate the Cu, it will decorate extrinsic loops. The gettering behavior of Fe is considerably more complex and Fe appears to decorate both open volume and interstitial-based defects if they coexist in one sample. Furthermore, the Fe profiles following annealing do not correlate particularly well with defect profiles visible by TEM, suggesting that Fe may decorate, or precipitate at, defects which are not easily observed by TEM.

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