SAND--97-1884C SAND97-1884C

COPPER IN SILICON: QUANTITATIVE ANALYSIS OF INTERNAL AND PROXIMITY GETTERING

CONF-970788--1

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Keywords: copper, silicon, gettering, implantation, oxygen precipitates, transient ion drift

Abstract

The behavior of copper in the presence of a proximity gettering mechanism and a standard internal gettering mechanism in silicon was studied. He implantation-induced cavities in the near surface region were used as a proximity gettering mechanism and oxygen precipitates in the bulk of the material provided internal gettering sites. Moderate levels of copper contamination were introduced by ion implantation such that the copper was not supersaturated during the anneals, thus providing realistic copper contamination/gettering conditions. Copper concentrations at cavities and internal gettering sites were quantitatively measured after the annealings. In this manner, the gettering effectiveness of cavities was measured when in direct competition with internal gettering sites. The cavities were found to be the dominant gettering mechanism with only a small amount of copper gettered at the internal gettering sites. These results reveal the benefits of a segregation-type gettering mechanism for typical contamination conditions.

Introduction

Copper is a prevalent contaminant in silicon with adverse effects on device performance. In spite of this fact, Cu is of particular interest for use as interconnect lines in semiconductor devices because of its low resistivity, however, these lines may act as a source for Cu contamination into the device region. Removal or gettering of Cu contamination out of the device region is highly desired, e.g. specifications for Cu contamination have dropped to 2.5×10^9 atoms/cm^2 [1]. A standard method to remove metal impurities from the near surface/device region is via internal gettering (IG) which utilizes oxygen precipitates in the material bulk [2, 3]. The limitation of IG is that it relies on impurity precipitation at the gettering site as well as impurity diffusion to the site. This creates the contradictory requirement of a low temperature anneal in order to create a supersaturation of the impurity in the silicon matrix leading to precipitation at the IG sites and a high temperature anneal for sufficient diffusion of the impurity. Additionally, contamination is often introduced into the silicon at the annealing temperature such that no supersaturation occurs. To obtain effective gettering under any annealing condition, "proximity" gettering methods located near the device region have been the focus of recent research with a particular interest in mechanisms which do not require an impurity supersaturation. One means to achieve proximity gettering is to use implantation species to getter the metal impurities in a region slightly deeper than the device region. Implantations with C, O, BF$_2$, N, Ge, Ne, Ar and B have been attempted, however, the gettering mechanisms either require impurity precipitation or are unstable at elevated temperatures [4-8]. A promising method uses cavities formed by He implantation which getter metal impurities on the unsaturated bonds of the cavity walls by chemisorption as well as metal-silicide precipitation when the surrounding silicon matrix becomes supersaturated with the metal impurity [6, 9-12]. The chemisorption mechanism is active without an impurity supersaturation and is stable at high temperatures with a reported binding energy of Cu to the cavity relative to Cu in solution of ≈ 2.2eV

[12], above the value for Cu-silicide precipitation, ≈1.5eV [13]. From these binding energies, one would expect less Cu remaining in the silicon matrix when cavities are present than with IG sites after an anneal. Furthermore, considering the cavities form a near continuous plane of sinks near the front surface while IG sites are more dispersed, an even lower impurity concentration would be expected in the device region when cavities are present as opposed to with only IG sites.

In the work presented here, our goal was to determine if the cavities significantly enhance gettering of Cu more than IG sites would getter by themselves. We have monitored Cu behavior in the presence of IG sites and He implantation-induced cavities with the use of secondary ion mass spectroscopy and transient ion drift. Moderate levels of Cu contamination were used such that the Cu was not supersaturated during annealing which provided realistic Cu contamination/gettering behavior. Quantitative measurements of Cu concentrations at both gettering sites were obtained after gettering anneals. Our results clearly demonstrate the advantages of gettering to cavities over IG sites.

Experimental Procedure

Boron doped <100>, 500μm thick CZ silicon with a resistivity of 10 Ω-cm and an initial oxygen concentration of $9x10^{17}/cm^3$ was used. All samples were subjected to a 1100°C, 5 hr anneal to create an ≈10μm denuded zone (DZ). Samples were prepared with and without internal gettering (IG) sites prior to forming the cavity gettering layers. IG sites were formed by a 700°C, 48 hours oxygen precipitate nucleation anneal, followed by a thermal ramp from 700 - 950°C in 50°C increments for 30 minutes each and finally with a 950°C, 8 hours precipitate growth anneal. All anneals were performed in a nitrogen atmosphere. The ramp step allows for oxygen precipitates to have a higher survival probability during the high temperature growth anneal and therefore provide a high concentration of internal gettering sites [14]. Laser Scattering Tomography (LST) measurements of defect densities revealed 10^{10} defects/cm^3 and $7x10^7$ defects/cm^3 for samples with and without the IG formation anneals, respectively. This provides a significant difference in IG site density between the two sample types. The interstitial oxygen (O_i) concentration was monitored with Fourier Transform Infrared Spectroscopy (FTIR) using the new ASTM standard in the as-grown state, following the DZ formation and after the IG formation anneals. No change in O_i was observed after the DZ formation but 10^{17} O_i atoms/cm^3 was precipitated during the IG formation anneal. Based on conservation of mass and the precipitate density measured with LST, a 10^{17} drop in O_i creates precipitates with radii of ≈35nm. To form the cavity gettering sites, He atoms were implanted at 300keV (≈1.35μm deep) with a dose of $1x10^{17}$ atoms/cm^2. $1x10^{14}$ Cu atoms/cm^2 were introduced ≈0.1μm deep on both the front and back sides by a 150keV implantation. The Cu was gettered by annealing the samples at either 700 or 800°C for 6 or 2 hours respectively in a vacuum furnace ($2x10^{-7}$ torr) with a slow cool to room temperature. Past work [9] has shown the cavities form within 30 minutes at 700°C, therefore ensuring the cavities are present and are active gettering sites for the majority of the gettering anneals. Secondary Ion Mass Spectroscopy (SIMS) was utilized to measure the Cu gettered by the cavities and, with the aid of statistical analysis, to roughly estimate the Cu gettered at the IG sites. High purity Float-Zone (FZ) silicon was used as a reference for both of these SIMS measurements. Additionally, the amount of Cu at the IG sites was measured with the use of a rapid thermal anneal with a rapid quench (RTAQ) at 1000°C for 45 seconds and measurements with the transient ion drift (TID) technique [15,16]. The quench rate is approximated as of 1000°C/sec. The RTAQ anneal is designed to dissolve the Cu from its original precipitation site which allows for TID to detect the interstitial Cu (Cu_i). TID exploits the capacitance change induced by the positively charged Cu_i drift in the depletion region of a Schottky barrier. The detection limit of TID is on the order of 10^{12} Cu_i atoms/cm^3 for these experiments. High purity FZ samples were subjected to the same 1000°C-45 sec anneal to act as reference samples. Al

evaporation was used to form diodes on all samples. Samples were cleaned prior to the RTAQ and diode formation with VLSI grade piranha (5:H_2SO_4:1H_2O_2), HF and high resistivity H_2O.

Results and Discussion

Figure 1 shows SIMS plot of the Cu distribution in the near surface region of a sample with IG sites. The sample has been subjected to a 800°C gettering anneal after He implantation to form cavities at $\approx 1.35\mu m$ and a Cu implantation at $\approx 0.1\mu m$ in order to intentionally contaminate the materials. Clearly substantial gettering of the Cu has occurred to the cavities. The SIMS results for cavity gettering at 700 and 800°C are summarized in the first column of Table 1. For both temperatures, the amount of Cu gettered to the cavities is hardly influenced by the presence or absence of the IG sites. It should further be noted that the measured amount is far below the level corresponding to saturation of the cavity wall sites, which for our experimental conditions is above 10^{15} atoms/cm^2 [12]. Also included in the table are the amounts of Cu remaining in the front and back near-surface layers where the Cu atoms were initially implanted. SIMS analysis was also performed deep in the bulk of the sample to determine the amount of Cu present at the IG sites. Although the dissolved Cu concentration was expected to be below the sensitivity of SIMS, it was hoped that extended SIMS profiling would reveal any Cu at IG sites via spikes in the Cu counts at depth intervals where IG sites are present. Figures 2a and 2b show deep SIMS profiles of samples after a 700°C gettering anneal with and without IG sites, respectively. The cavities and a

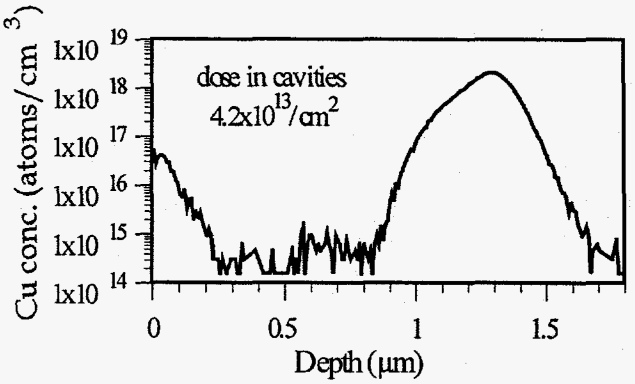
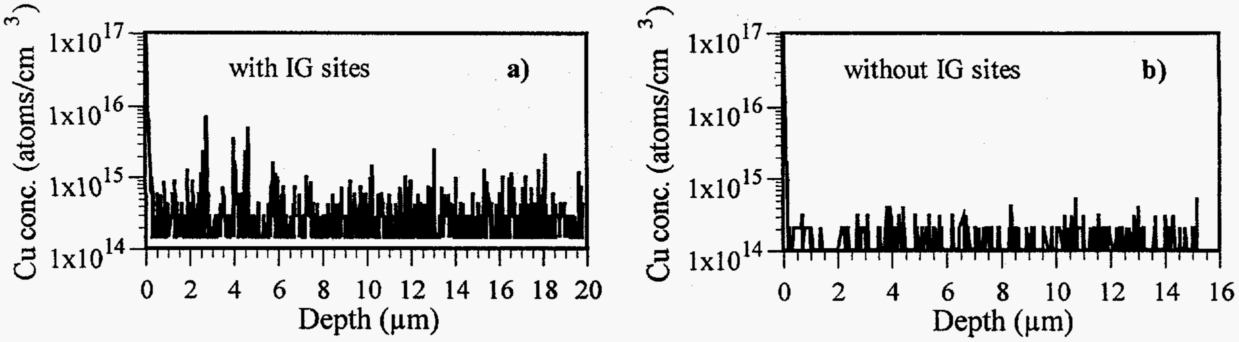


Figure 1: SIMS plots of front surface Cu distribution after a 800°C gettering anneal with IG sites and cavities. The cavity layer is at 1.35µm and the initial Cu implant was at 0.1µm.

Sample	Cu in cavities (10^{12} cm^{-2})	Cu in front (10^{12} cm^{-2})	Cu in back (10^{12} cm^{-2})	Cu in bulk (10^{12} cm^{-2})
with IG, 700°C	39	3.4	1.4	2-10 (SIMS) 12.5 (TID)
with IG, 800°C	42	0.3	1.8	-
no IG, 700°C	42	3.9	9.6	< DL (SIMS) < DL (TID)
no IG, 800°C	42	0.2	6.9	-

Table 1: Cu doses in the cavities, frontside, backside and bulk after 700 and 800°C anneals. DL = detection limit and - means sample was not measured.



Figures 2a&b: SIMS plots of Cu deep in the samples following a 700°C gettering anneal a) with and b) without IG sites. The cavities and a ≈150-200µm thickness has been removed prior to measurement.

≈ 150-200µm thickness of the underlying silicon wafer have been removed prior to the SIMS measurements via polishing and etching. Both profiles exhibit noise typical of SIMS data when the concentration of the detected isotope is near or below SIMS sensitivity. However, in the case of the specimen with more IG sites, there are additionally a number of spikes with large amplitudes, suggesting the presence of isolated agglomerations of Cu atoms within the matrix. This raises the possibility that a small fraction of the implanted Cu is gettered to bulk IG sites. A high purity float-zone (FZ) sample with no intentional Cu contamination was also subjected to deep SIMS analysis for comparison. The SIMS profile (not shown here) is similar to Figure 2b, the sample without IG sites.

To quantify the apparent spikes, we evaluated the statistical distributions of the SIMS yields in Figures 2a and 2b as well as the FZ SIMS data (not shown). These results were compared with the Poisson distribution expected for random noise with the same average number of counts per depth interval where counts are proportional to Cu concentration. Our findings are shown in Figures 3a and 3b, where the number of depth intervals yielding a particular number of SIMS counts is plotted

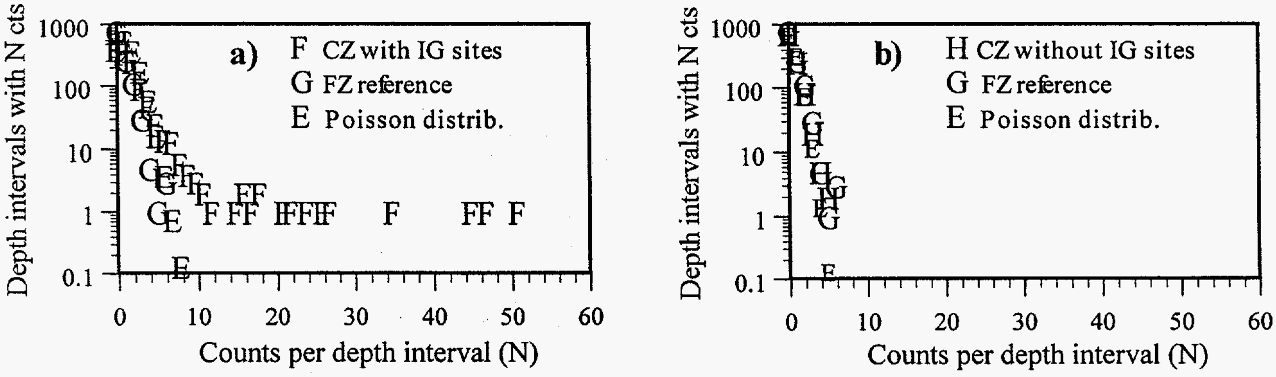


Figure 3a&b: Statistical analysis of data presented in Figure 2 and FZ SIMS data. The Poisson distribution approximates noise. Counts are proportional to Cu concentration. The CZ without IG sites and FZ reference data follows the Poisson distribution of noise.

versus the number of SIMS counts in the interval, denoted as N. The data from the specimen with few IG sites, Figure 3b, conforms well to the calculated Poisson distribution and the reference FZ silicon sample. In contrast, results for the sample with IG sites, Figure 3a, show a pronounced tail extending to large values of N. Moreover, when the number of spikes having amplitudes greater than random noise is divided by the sputtered volume, the resulting volume density is ≈2x10^9 cm^{-3}, or less than an order of magnitude smaller than the measured density of IG sites. In our view, this constitutes evidence for gettering of a small fraction of the implanted Cu by the IG sites. The amount of Cu in the spikes (at these IG sites) is ≈2-10x10^{12} atoms/cm^2 considering the area and depth probed with SIMS and the thickness of the silicon wafer, 500μm.

The 700°C gettered samples were polished and etched to remove the sputter pit formed by the deep SIMS analysis. Following extensive surface cleaning, the gettered samples were annealed at 1000°C for 45 seconds followed by a rapid quench to dissolve the Cu back into solution. High purity FZ samples were also annealed just prior and just after the gettered samples were annealed in order to check for contamination. This anneal has been used previously to dissolve precipitated Cu completely back into solution [16] and models of dissolution kinetics [17, 18] predict even a 4.4μm Cu_3Si precipitate would dissolve during this 1000°C-45 sec anneal. A precipitate of greater than this size is not expected to be present in the material. Therefore, we anticipate all Cu is dissolved back into solution after this anneal. Following surface cleaning and Al diode formation Transient Ion Drift (TID) measurements were performed on a number of diodes on the FZ reference samples and on the gettered samples. The results are shown in Figure 4. We see the sample with IG sites contains a significantly higher amount of Cu than the reference samples and the sample with no IG sites. This is consist with the deep SIMS profiling results. The measured concentration of 2.5x10^{14} Cu atoms/cm^3 is converted into a Cu dose of 12.5x10^{12} Cu atoms/cm^2, by simply considering the silicon samples are 500μm thick. This dose compares well with the dose of 2-10x10^{12} atoms/cm^3 measured with SIMS.

Summing the data in Table 1, we see a significant amount of the original Cu dose (2x10^{14} atoms/cm^2) has been lost during the annealing treatments. This is likely due to Cu evaporation from the silicon at elevated temperatures. Comparable rates of Cu evaporation have been previously observed under similar experimental conditions [12]. Additionally, previous work on Cu solubility in silicon have used vapor transport at temperatures as low as 650°C and anneal times comparable to those used in this study to intentionally contaminate silicon with Cu [19]. Based on these past works, the loss of Cu observed in this work is not a surprising phenomenon.

The information presented above is summarized in Table 1. We see the cavities getter the majority of the Cu regardless of the IG site density. The chemisorption process dominates the gettering action. It should be noted that the $\sqrt{Dt}$ product (where D is the Cu diffusivity and t is the anneal time) is 7700μm and 5700μm for the 700°C-6hr and 800°C-2hr anneal, respectively, which indicates both anneals provide time for significant Cu diffusion. Considering the implanted Cu will rapidly disperse throughout the 500μm thick silicon samples during the gettering treatments, a uniform distribution of 4x10^{15} Cu atoms/cm^3 is expected to form throughout the thickness of the material. Also, considering the solubility of Cu in the silicon matrix with respect to a Cu_3Si phase is 10^{16} and 7x10^{16} Cu atoms/cm^3 for the 700 and 800°C anneals respectively, the Cu is not supersaturated and no Cu would be expected to getter to the IG sites at the annealing temperature. This is a realistic scenario for Cu contamination since typically only small amounts of Cu are introduced into silicon during integrated circuit processing such that during an annealing the Cu is not supersaturated. However, the slow cool after the anneals allows for gettering of the Cu at the IG sites as it precipitates into Cu_3Si. Conversely, the cavities chemisorb Cu atoms during the anneal and during cooling as well act as a precipitation site for the Cu into the Cu_3Si phase just as the IG sites. Therefore, in these realistic contamination conditions, the cavities are the dominant gettering mechanism. Additionally, considering the close proximity of the cavities to the near surface region as compared to the IG sites and the fact that the cavities form a near continuous sheet of gettering sites while IG sites are more widely dispersed, one would expect the cavities to getter the device region much more effectively with short annealing sequences than the IG sites. Clearly cavity

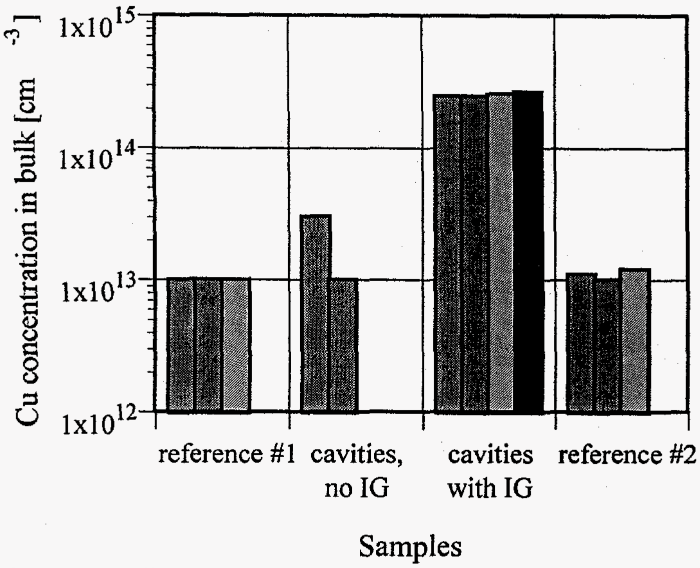


Figure 4: Bulk concentrations of Cu as measured with TID after an RTAQ at 1000°C for 45 sec. Reference samples determine the amount of contamination during the RTAQ.

formation is a worthwhile endeavor to ensure efficient gettering of Cu from the device region of silicon integrated circuits.

Conclusions

Gettering of Cu to He implantation-induced cavities and internal gettering sites was quantitatively analyzed for realistic Cu contamination scenarios. Novel SIMS profiling and data analysis and TID measurements allowed for the quantification of Cu at IG sites. The cavities effectively getter Cu in silicon even in the presence of internal gettering sites and the gettering action is dominated by the cavities. These results reveal the chemisorption mechanism of cavity gettering is a highly effective means for proximity gettering of metal impurities.

Acknowledgments

The authors would like to thank Dr. M. Werner and Dr. Kissinger for LST measurements and Dr. F. Kirscht for fascinating discussions. This work was supported by the U.S. D.O.E. under contract No. DE-AC04-94AL85000 and the Director, Office of Basic Energy Research, Materials Science Division, U.S. D.O.E. contract No. DE-AC03-76SF00098.

References

1. *The National Technology Roadmap for Semiconductors* (Semiconductor Industry Assoc., San Jose, CA 1994), p. 110
2. W. K. Tice and T. Y. Tan, *Mat. Res. Soc. Symp. Proc.* **2**, 367-380, 1981.
3. D. Gilles, E. R. Weber and S. K. Hahn, *Phys. Rev. Lett.* **64**, 196, 1990.
4. H. Wong, N. W. Cheung and P. K. Chu, *Appl. Phys. Lett.* **52**, 889-891, 1988.
5. W. Skorupa, R. Kogler, K. Schmalz, P. Gaworzewski, G. Morgenstren and H. Syhre, *Nuc. Instr. and Meth. in Phys. Res. B.* **74**, 70-4, 1993.
6. M. H. F. Overwijk, J. Politiek, R. C. M. d. Kruif and P. C. Zalm, *Nuc. Instr. and Meth. in Phys. Res. B.* **96**, 257-60, 1995.
7. C. J. Barbero, J. W. Corbett, C. Deng and Z. Atzmon, *J. Appl. Phys.* **78**, 3012-3014, 1995.
8. P. A. Stolk, J. L. Benton, D. J. Eaglesham, D. C. Jacobson, J.-Y. Cheng, J. M. Poate, S. M. Myers and T. E. Haynes, *Appl. Phys. Lett.* **68**, 51-3, 1995.
9. S. M. Myers, D. M. Follstaedt, D. M. Bishop and J. W. Medernach in *Proc. Semiconductor Silicon, 7th International Symposium on Silicon Materials Science & Tech.*, edited by H.R. Huff, W. Bergholz and K.Sumino, 1994, pg. 808
10. V. Raineri, A. Battaglia and E. Rimini, *Nuc. Instr. and Meth. in Phys. Res. B.* **96**, 249-252, 1995.
11. J. Wong-Leung, E. Nygren and J. S. Williams, *Appl. Phys. Lett.* **67**, 416-8, 1995.
12. S. M. Myers and D. M. Follstaedt, *J. Appl. Phys.* **79**, 1337-50, 1996.
13. E. R. Weber, *Appl. Phys. A.* **30**, 1, 1983.
14. S. A. McHugo, M. Mizuno, F. G. Kirscht and E. R. Weber, *Appl. Phys. Lett.* **66**, 2840, 1995.

15. T. Heiser and A. Mesli, *Appl. Phys. A.* **57**, 325, 1992.
16. T. Heiser, S. McHugo, H. Hieslmair and E. R. Weber, *Appl. Phys. Lett.* **70**, 3576-3578, 1997.
17. M. J. Whelan, *Metal Science Journal.* **3**, 95, 1969.
18. H. B. Aaron and G. R. Kotler, *Metal. Trans.* **2**, 393, 1971.
19. R. C. Dorward and J. S. Kirkaldy, *Trans. Metall. Soc.* **242**, 2055, 1968.