Gettering of copper impurity in silicon by aluminum precipitates and cavities

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Abstract Al precipitates as well as cavities (or open-volume defects) are known for their ability to getter impurities within Si. In order to compare their relative gettering strength we produced both Al precipitates and cavities at different depths within one Si wafer. This was done by H^+ and Al^+ implantation with different energies and subsequent annealing process, resulting in Al-Si alloy and cavities at depth of 300 nm and 800 nm, respectively. Cu was then implanted with an energy of 70 keV to a fluence of 1×10^{14}／cm^2. The Cu implanted samples were annealed at temperature from 700ºC to 1200ºC. It was found that Cu impurities were gettered primarily by the precipitated Al layer rather than by cavities at the temperature of 700~1000ºC, while gettering of Cu occured in both regions at the temperature of 1200ºC. The secondary ion mass spectrometry and transmission electron microscopy analyses were used to reveal the interaction between Cu impurities and defects at different trap sites.

Keywords Gettering, Ion implantation, Cavities, Al precipitates

CLC numbers O474, TN304.1$^+$2, TN305.3

1 Introduction

Transition metals are common impurities in silicon originating from the crystal growth and subsequently integrated circuits (IC) fabrication steps. They are typically detrimental and can cause degradation in the performance of electronic devices, e.g., reducing the minority carrier lifetime and increasing the junction leakage current.[1,2] The increasing complexity and miniaturization of modern integrated circuits require higher yield and hence a smaller density of defects and impurities in the electrically active zone of devices. Gettering is usually as an implemental role. There are mainly three approaches:[3] (1) to form a region with preferential nucleation sites for metal-silicide precipitation, such as point defects of SiO_2 precipitates (relaxation gettering),[4] (2) to create a zone with increased impurity solubility, such as Al-backside gettering (segregation gettering),[5] and (3) P-diffusion gettering, which involves dynamic processes arising from interstitial-defect gradients (injection gettering).[6]

Among these methods, segregation-induced gettering and injection-induced gettering remain active for most of metal impurities with any concentrations. Gettering of several transition metals by Al precipitates has been investigated previously. Copper in Si is shown to be effectively gettered by Al-rich precipitates.[7-9] Recently, a technique using microcavities or open-volume defects created by H or He ion implantation has been extensively studied and also shown to be effective for trapping Cu, Ni, Au and Pt in bulk Si.[2,10-12] The gettering efficiency of both Al precipitates and cavities as gettering sites for Cu-impurities is investigated in this paper.

2 Experimental

The silicon wafers used in our experiments were 3 inch diameter, (100), p-type, 8~14Ωcm. The following implantation procedure was performed within the same Si wafers:

(1) 3.5×10^{16} cm^{-2} of H^+ with the energy of 100 keV was implanted into the Si wafer followed by a 30

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min annealing at 500ºC, thus forming a band of cavities at the depth of the highest lattice damage (~ 0.8 μm) rather than at the depth of the H^+ projected range (~ 0.9 μm) calculated by TRIM 94 program;

(2) The Si samples, which underwent the treatment of process (1), were implanted with 1×10^{16} cm^{-2} of Al^+ at the energy of 180 keV, with the average projected range of Al^+ being about 300 nm. These samples were then annealed at 800ºC for 1 h to form Al precipitates near the depth of 300 nm;

(3) In order to study the distribution of Cu cavities and Al precipitates, copper was then implanted to a fluence of 1×10^{14} cm^{-2} with the energy of 70 keV. The projected range of the implanted Cu ions in Si is about 50 nm, which is much nearer to the surface than that of the Al precipitates and cavity band.

Then the above specimens were annealed at 700ºC, 1000ºC and 1200ºC, respectively, in N_2 atmosphere for 2 h in order to redistribute the implanted Cu impurities. N_2 was kept through the tube at a flow rate of 2 L·min^{-1} when the temperature was above 200ºC. The secondary ion mass spectrometry was used to measure the distribution of Cu from the Cu_3Si layer to the gettering sites. The O_2^+ ion beam with the energy of 15 keV was used for sputtering and analysis. Microstructure of the sample after 1000ºC annealing was examined by the cross-sectional transmission electron microscopy (XTEM) using a Philips CM200 FEG (field emission gun).

3 Results and discussion

Figs.1, 2 and 3 show the concentration profiles of the Al and Cu measured by SIMS after the final annealing at 700ºC, 1000ºC and 1200ºC, respectively. There are several Cu peaks in Fig.1. Since the Cu silicide was not fully removed by the gettering, the near surface peak *A*, in agreement with the projected range (R_p=50 nm) of 70 keV Cu ions simulated by TRIM94, accounts for the Cu precipitates confined near the surface after Cu^+ implantation and the following annealing. Without Al precipitates, Cu in the as-implanted sample should show a Gaussian distribution in the Si wafer. So other Cu-impurities peaks, which correspond to those in the Al concentration profile on the whole, establish that Cu-impurities are gettered by the Al-Si precipitates due to its higher solid solubility in Al-Si alloy than that in the silicide phase, although the gettering efficiency is not satisfying in comparison with the Cu concentration near the surface. No direct evidence can be observed that cavities also contribute to the Cu gettering in this phase. In Fig.2, the SIMS data show excellent proportionality between the concentrations of precipitated Al and gettered Cu at depth where Al is precipitated. On the contrary, there is only Al accumulating in the predicted gettering sites formed by H^+ implantation with very little Cu being gettered. Concentrations of Al accumulated among cavities are some lower than that of Al precipitates around the Al implantation region. It is clear that the gettering by precipitated Al is by far the dominant mechanism and precipitated Al is proved to strongly getter Cu from Cu_3Si in the 1000ºC case. If the first annealing had taken 10 h or longer instead of 2 h, it might have also shown the similar result as the latter experiment. Regardless, the chemical potential of the gettering sink formed by the precipitates is initially much lower than that of the silicide. However, the data in Fig.3 are significantly different from those in Fig.1 and Fig.2, showing the obvious transfer of Cu from the Al precipitates to open-volume defects. Some of Cu peaks, such as peaks *B*, *C* and *D*, are still induced by high concentrations of Al precipitates, but peak *E* in the region around 700 nm is undoubtedly related to the existence of cavities, for Al concentrations in this region do not differ much from those at the depth from 400 nm to 700 nm, from where no other high Cu yield is observed. This result indicates that Cu has almost equal preference for being gettered by either Al-Si alloy or open-volume defects in Si at 1200ºC. The reason for this transformation might be ascribed to the rise of temperature. With the temperature increasing, metal's diffusion coefficient improves as well, leading to an enhanced diffusion of Cu impurities and giving more chances for cavities to capture Cu impurities. Another proposed mechanism is that within the precipitated Al layers, as the Cu concentration increases, the chemical potential of Cu also increases. Initially, the chemical potential of Cu within the precipitated Al layers was higher than that within the cavities band. The high temperature of 1200ºC drove much more Cu impurities into the Al precipitated layer, leading to a significant increment of Cu chemical potential. So the chemical potential's difference between two layers results in a driving force for Cu to redistribute in the cavities. Above consideration was partially verified by the SIMS result in Fig.3, which indicated a fewer concentration of Cu impurities remaining in the near surface than in other two cases.

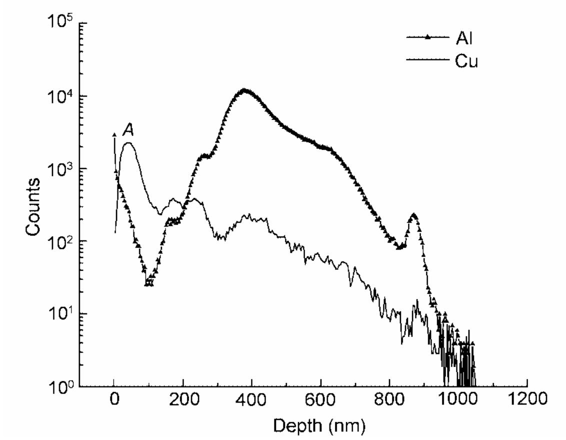

Fig.1 SIMS depth profiles of Al and gettered Cu in Si after annealing at 700ºC.

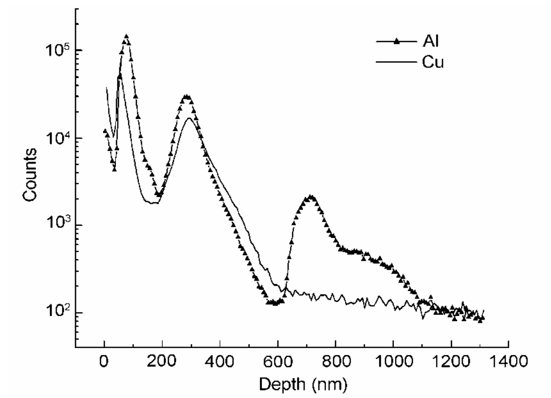

Fig.2 SIMS depth profiles of Al and gettered Cu in Si after annealing at 1000ºC.

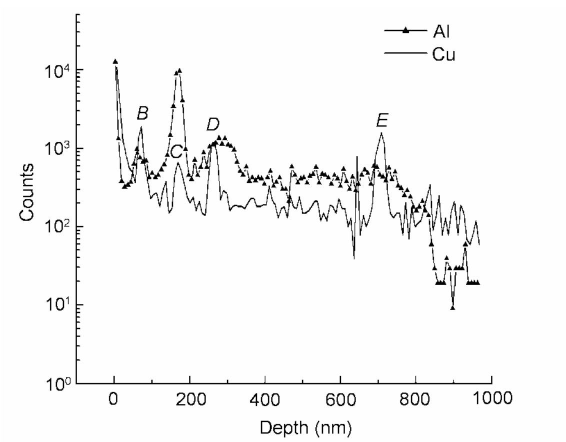

Fig.3 SIMS depth profiles of Al and gettered Cu in Si after annealing at 1200ºC.

Moreover, though Al-Si alloy can get rid of some metal impurities effectively, it is not easy to locate Al precipitates at a definite depth. The Al concentration profile changes greatly with temperature and annealing time referring to the SIMS data and Al precipitates exist within a wide range. By comparison, cavities remain at approximately the same depth.

An XTEM micrograph for a 1000ºC annealed sample is shown in Fig.4. The image clearly reveals two gettering sites formed by Al^+ implantation and H^+ implantation, respectively, and Cu precipitates that were generated by the Cu^+ implantation and subsequent annealing. An example of the identified cavities, situated in about 800 nm below the surface, is marked on the left side of the figure with "C". Although clear presence of mass cavities is not observed in our XTEM images, we do find some isolated cavities within the band (as shown in Fig.5). This void, obviously has evolved into a faceted shape, is as large as 35 nm and filled with Al precipitates. Unexpected decrease in cavity amounts can be probably attributed to our technical limitation as well as to the Al-implanted induced strain in silicon and the transfer of Al to this region. Besides cavities, there are other defects around this region like dislocations. But that Cu impurities have a high preference for decorating open-volume defects rather than dislocations described by others is seen.[13] So we consider cavities as dominant mechanism for gettering Cu impurities in this region. Fig.6 is a high resolution XTEM image of the near surface region, showing the small Cu:Si precipitate colony nucleated at the stair-rod dislocation of stacking fault tetrahedral (SFT) induced by Cu implantation after annealing. This relatively large quantity of Cu:Si precipitates serves as the silicide source to the gettering sink in our experiment.

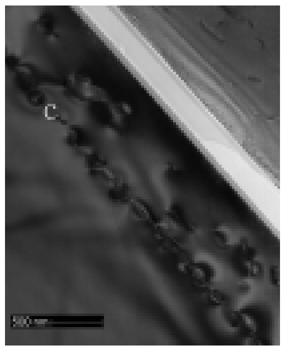

Fig.4 An XTEM micrograph illustrating defects in Cu-implanted samples following annealing at 1000ºC.

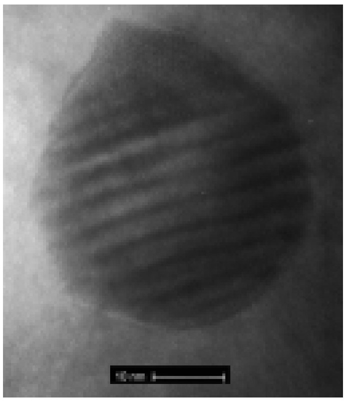

Fig.5 High resolution XTEM image of a cavity.

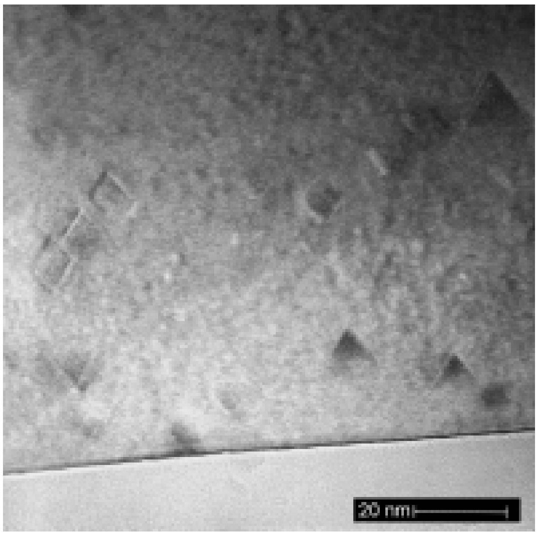

Fig.6 High resolution XTEM micrograph of near surface region after annealing at 1000ºC for 2 h.

4 Conclusions

By means of detailed SIMS and XTEM investigations, the gettering behavior of Cu in Si was studied. This study was performed on a single wafer, which contained laterally different regions with Al-Si alloy, open-volume defects and impurities. At temperature below 1000ºC, it is clearly shown that Cu-impurities have a high preference for being gettered by Al-Si alloy. On the other hand, Cu-impurities will redistribute in both Al-Si alloy and open-volume defects at 1200ºC. These results suggest that the use of both Al precipitates and open-volume defects is technologically attractive for the applications requiring the removal of Cu impurities.

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