Comparison of Cu gettering to H⁺ and He⁺ implantation-induced cavities in separation-by-implantation-of-oxygen wafers

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(Received 30 December 1997; accepted for publication 18 September 1998)

Well-defined bands of cavities have been formed beneath the buried oxide (BOX) layer of two sets of separation-by-implantation-of-oxygen (SIMOX) wafers by H⁺ and He⁺ implantation. The gettering of Cu impurities, which were implanted into the top Si layer at different doses (5×10^{13} , 5×10^{14} , and 5×10^{15} /cm²), to the cavities has been studied by secondary ion mass spectroscopy and cross-sectional transmission electron microscopy. The results indicated that the cavities induced either by H⁺ or He⁺ implantation are effective gettering centers for Cu in SIMOX wafers, and up to 4×10^{15} /cm² Cu has diffused through the BOX layer and been captured by the cavities. The gettering efficiency of cavities increases with the decrease of Cu implantation doses and the increase of annealing temperatures. He⁺ ion implantation. © *1999 American Institute of Physics*. [S0021-8979(98)06524-4]

I. INTRODUCTION

Silicon on insulator (SOI) is an attractive technology for low power, low voltage, and high speed electronics^{1,2} and separation-by-implantation-of oxygen (SIMOX) is one of the most important SOI fabrication technologies. During the fabrication of SIMOX wafers, however, metal impurities may be introduced into the wafers. Because the presence of a high concentration of metals in the top Si layer of SIMOX will deteriorate devices built into this region,^{3,4} the metal impurities must be removed from the top Si layer. The gettering processes in SOI wafers are very different from conventional gettering schemes developed for bulk silicon materials. The presence of the buried oxide (BOX) layer, which is located between the top Si layer and the Si substrate to provide electrical isolation of the top Si layer from the silicon substrate, introduces a barrier to traditional internal or backside gettering sites. It has been reported that the intrinsic implantation damage in SIMOX wafers can serve as gettering sites for the transition metals.^{5–7} However, the gettering efficiency of such intrinsic gettering sites varies with the SIMOX fabrication process used and there is no effective gettering in the BOX of bonded SOI.⁶ Therefore, more favorable trapping sites should be introduced to reduce the concentration of metal impurities in the top Si layer to an acceptable level.

Cavities induced by H^+ or He^+ implantation and the subsequent annealing are found to be strong gettering sites for transition metal impurities such as Cu, Ni, etc. in bulk Si.^{8–11} In a previous study,¹² we introduced the cavities by hydrogen implantation into the Si substrate of a low-dose SIMOX wafer, and found that the gettering efficiency of the H^+ implantation-induced cavities is much stronger than that of the intrinsic gettering sites, and that 73.6% of the initial 5×10^{15} /cm² Cu implants (corresponding to a dose of 3.6 $\times 10^{16}$ /cm² Cu) was trapped from the top Si layer to the cavities after the 1000 °C annealing. In the present study, the gettering effect of the Cu impurities, which had been implanted into the top Si layer at doses of 5×10^{13} , 5×10^{14} , and 5×10^{15} /cm², respectively, to the cavities in low-dose SIMOX and high-dose SIMOX wafers has been investigated. Our results demonstrate that the cavities induced both by H⁺ and by He⁺ implantation are effective gettering sites for Cu in SIMOX wafers of different structures.

II. EXPERIMENTAL PROCEDURE

Two sets of SIMOX wafers were used in this study. The first set of SIMOX wafers (No. 1 SIMOX) was fabricated by a high dose of O^+ implantation $(1 \times 10^{18}/cm^2)$ and subsequent annealing. The thicknesses of the top Si layer and the BOX layer in the No. 1 SIMOX wafer are 70 and 210 nm, respectively. The second set of SIMOX wafers (No. 2 SI-MOX) was a low-dose SIMOX, which was implanted with 3.3×10^{17} /cm² O⁺ at 70 keV and annealed at 1300 °C for 5 h, resulting in a thinner BOX layer 70 nm thick with an overlayer of 110 nm. Next 4×10^{16} /cm² H⁺ ions were implanted into the Si substrate of No. 1 SIMOX at an energy of 70 keV, where the cavities were located 660 nm below the sample surface. The No. 2 SIMOX wafer was implanted with 9×10^{16} /cm² He⁺ ions at 60 keV (Rp = 500 nm). These two sets of wafers were subsequently annealed at 700 °C for 30 min to drive the gases out of the cavities. Then the No. 1 SIMOX wafer was implanted with 5×10^{13} /cm² (No. 1a) and $5\!\times\!10^{14}\!/\text{cm}^2$ (No. 1b) Cu^+ ions at 70 keV, and 5 $\times 10^{15}$ /cm² of Cu⁺ ions was implanted into the top Si layer of the No. 2 SIMOX at 70 keV (No. 2a). All the H⁺, He⁺,

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FIG. 1. SIMS profiles of Cu before and after annealing for the H⁺ (4 $\times 10^{16}$ /cm², 70 keV) and Cu⁺ (5 $\times 10^{13}$ /cm², 70 keV) implanted No. 1 SIMOX sample: (a) as implanted, (b) annealed at 700 °C for 2 h, and (c) annealed at 1000 °C for 2 h.

and Cu⁺ implantations in this study were performed at room temperature. Finally, the samples were annealed at 700 and 1000 °C for 120 or 90 min in flowing N₂. The Cu distributions and the microstructures of the specimens were characterized by secondary ion mass spectroscopy (SIMS) and cross-sectional transmission electron microscopy (XTEM), respectively.

III. RESULTS AND DISCUSSION

The SIMS results of No. 1a, which had been implanted with 4×10^{16} H/cm² and 5×10^{13} Cu/cm², are reported in Fig. 1. The O profile indicates that a BOX layer of good quality has been formed in the No. 1 SIMOX wafer. Before annealing the implanted Cu is confined in the top Si layer [Fig. 1(a)]. The H profile in this sample gives a small peak at the cavity band, indicating that the 700 °C annealing per-



FIG. 2. SIMS profiles of Cu before and after annealing for the H⁺ (4 $\times 10^{16}$ /cm², 70 keV) and Cu⁺ (5 $\times 10^{14}$ /cm², 70 keV) implanted No. 1 SIMOX sample: (a) annealed at 700 °C for 2 h and (b) annealed at 1000 °C for 2 h.

formed between the H⁺ and Cu⁺ implantations has caused most of the implanted H to diffuse from the bubbles, leaving a small amount of H in the cavity band. This result is in agreement with the literature.8 Interestingly, we detected a large amount of H in the BOX layer of this sample, suggesting that the BOX layer of the SIMOX wafer can easily capture the H diffusing in it. After the No. 1a sample was annealed at 700 °C for 120 min [Fig. 1(b)], the Cu began to redistribute from its original peak and 66% of the totally implanted Cu diffused through the BOX layer and was situated at a depth corresponding to the original H distribution, indicating that the BOX layer in the SIMOX material does not prevent the diffusing of Cu at temperatures above 700 °C. After the 700 °C annealing, 17% of the Cu was in the BOX layer, with 14% of the Cu remaining in the top Si layer. Increasing the annealing temperature to 1000 °C resulted in 1% of the Cu remaining in the top Si layer and 6.4% of Cu accumulated in the BOX layer. Most of the Cu (92%) was captured in the cavities.

Figure 2 exhibits the Cu distribution profiles of the No. 1b sample, in which the implanted Cu dose is an order of magnitude higher than that in the No. 1a sample. Following the 700 °C annealing, about 68% of the Cu remained in the sample surface, and only 32% of the implanted Cu had diffused inward and been captured by the BOX layer and cavities. The amount of Cu left in the top Si layer decreases with increasing annealing temperatures. After the No. 1b sample was annealed at 1000 °C for 120 min, about 96% of the Cu had left the top Si layer. Ten percent of the Cu accumulated

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FIG. 3. SIMS results of No. 2a SIMOX wafer, which was implanted with 9×10^{16} /cm² He⁺ and 5×10^{15} /cm² Cu⁺ and annealed at (a) 700 and (b) 1000 °C for 90 min.

in and near the BOX layer and more than 86% of the Cu was trapped by the cavities.

A dose of 9×10^{16} /cm² He⁺ was implanted into the Si substrate of the No. 2 SIMOX wafer followed by a 700 °C annealing in order to form a cavity band beneath the BOX layer. Then a high dose of Cu impurities $(5 \times 10^{15}/\text{cm}^2)$ was intentionally introduced into the top Si layer by ion implantation. The Cu distribution in this sample after annealings at 700 and 1000 °C for 90 min is illustrated in Fig. 3. The gettering behavior of He⁺ implantation-induced cavities is similar to that of the H⁺ implantation-induced cavities. After the 700 °C annealing [Fig. 3(a)], Cu diffused away from the surface and accumulated in three regions: about 28% of the Cu remained near the surface of the top Si layer, 40% of the Cu precipitated at the lower interface of the BOX and in the thin Si layer just beneath the BOX, and 32% of the Cu was gettered in the cavity band. For the 1000 °C annealed sample [Fig. 3(b)], the proportion of Cu trapped by the cavities increased to 80%, corresponding to a dose of 4×10^{15} /cm². There was still 15% of the Cu remaining in the top Si layer and 5% of the Cu accumulated in the BOX layer.

Figure 4(a) shows the XTEM image of the No. 2a SIMOX sample after heating at 1000 °C for 90 min. The Cu implantation dose of 5×10^{15} /cm² is high enough to create an amorphous layer around the projected range. In Fig. 4(a) some residual defects and Cu precipitates can occasionally be observed in the top Si layer. The electron diffraction of this region in Fig. 4(b) exhibits elongated spots and a ring pattern in addition to sharp spots. This suggests that the Cu implantation-induced amorphous region has not completely recovered to a perfect crystal after the 1000 °C annealing. The damage caused by the lower dose of Cu implantation in



FIG. 4. (a) XTEM image of No. 2a SIMOX wafer implanted with 9 $\times 10^{16}$ /cm² He⁺ and 5 $\times 10^{15}$ /cm² Cu⁺, followed by annealing at 1000 °C for 90 min. (b) The electron diffraction pattern from the near surface region of the top Si layer of No. 2 SIMOX wafer after annealing at 1000 °C for 90 min.

Nos. 1a and 1b is not too severe and can be removed by the 1000 °C annealing. A cavity band 200 nm width has formed beneath the BOX layer [Fig. 4(a)]. It can be seen that the cavity density in the lower part of the cavity band is higher than that in the upper part. In accordance with this observation, the SIMS analysis in Fig. 3(b) shows that the Cu concentration at the lower part of the cavity band is evidently higher than that in the upper part. Most of the large cavities are faceted while the shape of the small cavities is spherical. No bulk Cu₃Si phase was observed in the cavities in Fig. 4(a). The average diameter of the cavities is about 30 nm and the areal density of the cavities is around $2 \times 10^{11}/\text{cm}^2$. As-

suming that there are seven Si bonds/nm² on the cavity surface,¹³ the trapping sites available on the cavity walls per wafer area after the 1000 °C annealing are calculated to be 3.5×10^{15} /cm², with an uncertainty about 20%. It has been proposed that when the Cu dose exceeds a monolayer coverage at the cavity walls, the bulk phase may nucleate in cavities.⁸ Our observations support this conclusion. In this study, no silicide precipitates were observed in the cavities of any of the samples where the amount of Cu trapped in the cavity band was less than or close to the calculated gettering sites on the cavity walls. In previous work,¹² the authors found, that when the Cu trapped in the cavity band (3.6 $\times 10^{15}$ /cm²) far exceeded the trapping sites (about 2 $\times 10^{15}$ /cm²) on the cavity walls, the bulk phase formed in the cavities.

It is well known that each gettering process should consist of three steps:¹⁴ impurity release from the impurity source, impurity transportation to the gettering sites, and impurity trapping or precipitation at the gettering sites. Based on the results in this study, we propose the following trapping mechanism for Cu in the top Si layer of SOI wafers for the cavities beneath the BOX layer. After implantation, the Cu concentration in the near surface greatly exceeds the equilibrium solubility and the near surface of the top Si layer is heavily damaged. These implantation-induced defects act as gettering sites for Cu.⁸ The as-implanted Cu is most likely present in three forms: captured by the implantation-induced defects, in the form of Cu precipitates, and dissolved in the lattice. Upon heating, Cu is gradually released from the Cudefect complexes and diffuses across the BOX layer to the cavity band. Cu is the fastest diffusing impurity in Si and can easily diffuse through the BOX layer of SIMOX wafers at temperatures above 700 °C. The dangling bonds on the cavity walls are highly active and the Cu diffusing into the cavity band will be strongly captured.¹³ Thus the Cu concentration in solution near the cavities is decreased and a negative Cu concentration gradient in the solute near the cavities is formed. This negative gradient results in the further dissolution of Cu from the original impurity source and transportation to the cavities. This process will not stop until the cavities are saturated or until no more Cu impurities are released from the Cu-defect complexes. When the Cu impurities diffuse through the BOX layer, some Cu is captured by the defects in the BOX layer. Our observations demonstrate that the gettering efficiency of the defects in the BOX layer is much lower than that of the cavities.

XTEM examination indicated that the total internal surface of the cavities decreases with increasing annealing temperature above 700 °C. In the present study, however, we found that the gettering efficiency of the cavities increased when the annealing temperature was increased from 700 to 1000 °C. This phenomenon most probably results from the release of Cu from the implantation-induced defects at different temperatures. Ion implantation-induced damage can act as a gettering site for transition metals.^{8,15,16} Only the Cu in solution can be transported to the cavities by diffusion. Higher temperature annealing will cause more Cu to be released from the Cu-defect complexes. Following thermal treatment at 1000 °C, almost all of the implanted Cu impurities in Nos. 1a and 1b were released from their original damage and diffused inwards to be captured by the more stable gettering centers (in this case trapped by the cavities), while the surface disorder of the No. 2a sample induced by higher dose Cu implantation cannot be annealed out completely. A fraction (15%) of the implanted Cu was still captured by the residual defects not removed by the 1000 °C annealing.

Our experiments demonstrate that both the H^+ and He^+ implantation-induced cavities are effective gettering sites for Cu in SIMOX wafers, and that these cavities can trap a high dose of Cu $(3.6 \times 10^{16} \text{ Cu/cm}^2 \text{ for H}^+ \text{ induced cavities}^{12} \text{ and}$ 4×10^{16} Cu/cm² for He⁺ induced cavities) from the top Si layer. From the point of view of cavity formation, we suggest that He⁺ implantation is more suitable for metal impurity gettering than H⁺ implantation. He⁺ ions implanted at doses from 2×10^{16} to 1×10^{17} /cm² can produce continuous cavities in Si without delaminating the surface Si.¹³ However, H⁺ implantation at doses higher than 4×10^{16} /cm² will result in the surface Si blistering and splitting from the substrate.¹⁷ This property of H⁺ implantation makes it more suitable for the Smart-Cut process¹⁸ than impurity gettering. On the other hand, H⁺ implanted at doses lower than 4 $\times 10^{16}$ /cm² cannot generate continuous cavities in Si.

IV. CONCLUSIONS

In summary, the gettering of Cu to cavities induced by H^+ and He^+ implantation has been studied. The results demonstrate that both H^+ and He^+ implantation-induced cavities are effective gettering sites for Cu impurities in SIMOX wafers of different structures. The gettering efficiency of the cavities increases with decreasing Cu implantation dose, and increases with increasing annealing temperature. Up to 4×10^{16} /cm² of Cu has been captured by the cavities in a SIMOX wafer after annealing at 1000 °C. Cavity gettering provides a promising way for removing Cu impurities from the top Si layer of SIMOX wafers. Since it is difficult for H^+ to produce continuous cavities without delaminating the surface layer, He^+ ion implantation may be more suitable for cavity formation and gettering.

ACKNOWLEDGMENT

This work was supported by the Shanghai Research Center for Applied Physics.

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