Gettering of Cu by He-induced cavities in SIMOX materials

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Abstract

Gettering of Cu impurities to He-implantation induced cavities in separation by implantation of oxygen (SIMOX) materials has been investigated by means of cross-sectional transmission electron microscopy and secondary ion mass spectroscopy. The cavities were introduced beneath the buried oxide layer (BOX) in SIMOX substrates by He+ implantation (9 × 10^{16}/cm², 60 keV) and subsequent annealing. The results indicate that these cavities are strong gettering sites for Cu impurities which have been implanted into the top Si layer of SIMOX. After a 1000°C annealing, 80% of the initially implanted Cu impurities in the top layer have diffused through the buried oxide layer to be captured by the cavities. The gettering effect of these He-induced cavities is much stronger than the damage region beside the BOX. The buried oxide in SIMOX does not appear to prevent the movement of Cu at 1000°C. He+ implantation-induced cavity has been demonstrated to be an attractive method to remove Cu impurities away from the top Si layer in SIMOX wafers.

1. Introduction

Metallic impurities, such as Cu, Ni and Au, can act as generation recombination (GR) centers within the bandgap. The GR centers presented in the active region of integrated circuit (IC) devices can increase the leakage current and reduce the minority carrier life time, thereby dramatically degrading the quality of devices [1]. Gettering is a useful technique to remove metallic impurities from the active region to favorable trapping or precipitation sites. Recently, it has been found that cavities (voids) induced by H+ or He+ implantation and subsequent annealing can effectively getter transitional metal impurities such as Cu, Ni, etc in bulk Si [2–5]. This gettering method has the advantage of high gettering efficiency and high stability at high temperature [5].

SIMOX (separation by implantation of oxygen) materials have a number of advantages for fabricating complementary metal-oxide-semiconductor (CMOS) devices, such as radiation hardness, high...
speed performance, and high temperature operation [6,7]. During the fabrication of SIMOX, however, metal impurities are easily 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 [8,9], the metals must be removed away from the top Si layer.

In this paper, a cavity band has been introduced in the Si substrate of SIMOX by He$^+$ implantation and subsequent annealing, and the gettering of copper to such a cavity band in SIMOX materials has been studied. The samples were characterized by cross-sectional transmission electron microscopy (XTEM) and secondary ion mass spectroscopy (SIMS). Our results demonstrate that after annealing in the temperature range of 700–1000°C, the implanted Cu in the top Si layer has diffused through the BOX and been strongly gettered by the cavities in the Si substrate.

2. Experimental

Device grade n-type Si wafer of (1 0 0) orientation was implanted with 70 keV oxygen ions at a dose of $3.3 \times 10^{15}$/cm$^2$. During implantation, the wafer was maintained at 600°C. After implantation the wafer was annealed at 1300°C for 6 h in N$_2$ ambient.

The formed SIMOX wafer was firstly implanted with $5 \times 10^{15}$/cm$^2$ Cu$^+$ and then with $9 \times 10^{16}$/cm$^2$ He$^+$ at room temperature. The ion energies for Cu$^+$ and He$^+$ implantation were 70 and 60 keV, respectively. All the implantation was performed at an angle of about 7° from the surface normal, in order to avoid ion channeling. There was no annealing between these two implantation. The Cu, He co-implanted SIMOX wafer was then cut into small pieces to be annealed in the temperature range of 700–1000°C in N$_2$ ambient for 90 min. In order to demonstrate the gettering effect of Cu to cavities in SIMOX more clearly, a SIMOX wafer only implanted with Cu was also annealed at 1000°C.

The Cu distribution in the Cu-implanted and Cu, He co-implanted SIMOX wafers, which have been annealed at various temperatures, were measured by SIMS with a CAMECA IMS-3F ion microanalyser using a 15 keV O$_2^+$ beam, and the depth calibration was done by measuring the sputtered crater with a stylus method. The structure of the 1000°C annealed Cu, He co-implanted SIMOX wafer was studied by XTEM with specimen prepared by mechanical thinning followed by argon ion beam milling.

3. Results and discussion

Fig. 1 shows the XTEM image of the Cu, He co-implanted SIMOX sample after annealing at 1000°C for 90 min. The SIMOX substrate consists of a buried stoichiometric SiO$_2$ layer, about 80 nm, and an over layer of 120 nm of single crystal silicon. Cu was implanted into the near surface of the top Si layer. After this 1000°C annealing, some precipitates, which appear as dark grains, have been observed near the surface (not shown in this figure). Such precipitation was identified to be
Cu$_3$Si in a previous study of Myers and Follstaedt [10]. Beneath the BOX layer, a cavity band wide of 200 nm has been formed at a depth of 500 nm from the surface, by He$^+$ implantation and subsequent annealing. The diameters of the cavities vary from 10 to 60 nm. It can be seen that the cavity density in the lower part of the cavity band is bigger than that in the upper part.

The SIMS results of Cu-implanted SIMOX sample before and after annealing are given in Fig. 2. Here the O profile is shown for depth comparison. In the Cu as-implanted SIMOX, Cu is mainly present near the surface (Fig. 2(a)). After an 1000°C annealing, the implanted Cu impurities begin to redistribute, as shown in Fig. 2(b), and the Cu profile exhibits two peaks. Peak A is located near the surface, and decays almost exponentially with depth. Peak B situates at the lower SiO$_2$/Si interface and can be attributed to metal segregation at substantial crystal damage in this region. In addition to these two peaks, Cu yield in the Si substrate just beneath the BOX layer is also high, indicating that some of the implanted Cu impurities have been trapped there. However, no defects can be observed in this region by XTEM in this study. The observed impurity segregation in this region may be related to the strain which arises from the formation of the BOX layer. The gettering of Cu to the interfaces of the BOX layer and to the thin Si substrate beneath the BOX layer has been observed by Kamins and Chiang [11] and Jablonski et al. [12]. The metal yield in the BOX is much lower. Therefore, most of the Cu not in the near surface peak has been captured by the lower SiO$_2$/Si interface. These results indicate that both the residual irradiation damage induced by Cu$^+$ implantation and the damage regions around and beneath the BOX layer are gettering sites for the implanted Cu impurities.

Fig. 3(a)–(c) illustrates the SIMS depth profiles of the Cu, He co-implanted SIMOX wafers annealed at different temperatures. Obviously, upon annealing, Cu distribution in the Cu, He co-implanted SIMOX (Fig. 3) is significantly different from the Cu implanted sample, as shown in Fig. 2(b). In all of the three figures in Fig. 3, there exists a Cu peak at the depth of the cavity band. After annealing at 700°C for 90 min (Fig. 3(a)), Cu starts to redistribute from the surface and presents at three regions: about 28% of the Cu remains at the near surface of top Si, totally 40% of the Cu presents at the lower interface of the BOX and in the thin Si layer just beneath the BOX, and 32% of the Cu is gettered by the cavity band. Increasing the annealing temperature, more Cu impurities diffuse through the BOX layer and are trapped at the cavity band. For the 800°C and 1000°C annealed sample, the Cu amount pre-
sents at the cavity band is 61% and 80%, respectively. A summary of Cu distribution for Cu-implanted and Cu, He co-implanted samples annealed at different temperatures was given in Table 1.

Comparing the SIMS results of the Cu-implanted, 1000°C annealed sample (Fig. 2(b)) with that of the Cu, He co-implanted and 1000°C annealed sample (Fig. 3(c)), we can see that the Cu distribution for these two samples are quite different. For the Cu implanted sample, 55% of Cu remains in the top Si layer, the rest of Cu has diffused through the BOX layer and been trapped at the lower BOX interface. For the Cu, He co-implanted SIMOX which has a cavity band in the Si substrate, 80% of Cu was captured by cavity band, only 15% of the Cu was left in the irradiated defect region in the top Si layer, and 3% of Cu located in the BOX layer. No Cu segregated around the BOX. These results allow the conclusion that comparing with the Si/SiO2 interface damage and the strain beneath the BOX, the He implantation induced cavities are stronger gettering sites for Cu in SIMOX. It has been proposed that the dangling Si bonds on cavity walls are highly reactive and trap some metal impurities, such as Cu, strongly by chemisorption [2,4,13]. Our results support this suggestion. We found that almost all of the Cu diffused through the BOX layer has been attracted to the cavity band. The existence of 15% of Cu in the top Si layer in Fig. 3(c) suggests that the Cu irradiated damage has not been totally annealed out at 1000°C and some Cu impurities are still captured by the residual defects.

In addition to the observation of Cu gettering to cavities, we also found that the Cu peak in the top Si layer out-diffused to the sample surface upon annealing at 1000°C, as a result, some Cu evaporated from the surface, this is in good agreement with Ref. [10]. For the 700°C and 800°C annealed samples, however, the Cu out-diffusion and evaporation have not been observed in this study. Shabani et al. [14] have found that for the SIMOX wafer which was contaminated with Cu by spin coating, the Cu loss did not occur until it was annealed at 1325°C. These results indicate that the Cu evaporation at sample surface strongly depends on the actual experimental condition.

4. Conclusion

In conclusion, a cavity band has been introduced in the substrate of SIMOX by He⁺ implantation and subsequent annealing. High dose of Cu (5 x 10¹⁵/cm²) has been implanted into the top silicon layer of SIMOX wafer. The gettering effect of Cu to these cavities has been studied. For the SI-
MOX wafer implanted only with Cu and annealed at 1000°C, 45% of the implanted Cu has been diffused through the BOX and been captured by the damage at the lower Si/SiO₂ interface and by the thin strain layer beneath the BOX layer, with 55% of the implanted Cu left in the top Si. In the SIMOX wafer co-implanted with Cu and He, the cavities formed in the Si substrate act as strong gettering sites for Cu. After a 1000°C annealing, 80% of the implanted Cu has been trapped by the cavities. The gettering effect of these He-induced cavities is much stronger than the damage region beside the BOX layer.

References


Table 1
Cu distribution in Cu-implanted and Cu, He co-implanted SIMOX samples annealed at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Cu in top Si layer (%)</th>
<th>Cu at cavity band (%)</th>
<th>Cu at regions in/around BOX (%)</th>
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<tbody>
<tr>
<td>Cu- implanted</td>
<td>Unanneled</td>
<td>100</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>1000</td>
<td>55</td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td>Cu, He implanted</td>
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<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>700</td>
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