Effect of the tilt angle on antimony in silicon implanted wafers

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A dose of 5.0×10^{14} antimony (Sb^+) ions cm^{-2} was implanted into silicon wafers at an energy of 70 keV, at different tilt angles (0° , 15° , 30° , 45° , and 60°). One set of samples was preamorphized with 160 keV germanium (Ge^+) ions with a dose of $1 \times 10^{15} \text{ cm}^{-2}$. The second set consisted of implants into single crystal silicon. After implantation the samples were annealed at 700°C for 30 s in a pure nitrogen ambient. Secondary ion mass spectroscopy was performed to evaluate the atomic profile and the retained dose as a function of the tilt angle before and after annealing. Rutherford backscattering spectroscopy and ion channeling measurements were performed to quantify the retained dose and the substitutional fraction of antimony in the preamorphized and crystalline samples. Hall measurements were performed in order to calculate the proportion of the dopant which was electrically active. It was found that the substitutional fraction was a function of the tilt angle for all of the implanted samples. A correlation was also found between the electrical activation and the substitutional fraction with the highest electrical activation being found at 15° tilt (90% for antimony implants into crystalline silicon) and 0° tilt (94% for antimony implants into amorphous silicon). For all implant angles the substitutional fraction and dopant activation was greater for the implants into amorphized silicon than for those into the crystalline phase. © 2004 American Institute of Physics. [DOI: 10.1063/1.1702096]

INTRODUCTION

In modern ultralarge scale integrated circuit technology, ion implantation has become the major technique for doping semiconductor devices.^{1,2} In many cases the functionality of the device depends on a precise control of ion dose and tilt angle. Nowadays high angle implants have become more and more important for deep submicron devices.³ Wafers are routinely implanted with doses that exceed the equilibrium solid solubility of the implanted atom in silicon. The electrical activation is correlated to the fraction of the dopant that is located in substitutional sites in the silicon lattice. A technique which is capable of quantifying the substitutional fraction of a dopant in ion implanted silicon is Rutherford backscattering spectroscopy (RBS) and ion channeling.⁴

We have carried out a detailed study of the effect of the angle of incidence on the atomic and electrical profiles of the important dopants, namely: arsenic, boron, and antimony implanted into both amorphous and crystalline silicon. While arsenic and boron ions are the most common *n* and *p* type dopants, phosphorous and antimony are also used as *n*-type dopants. In particular, antimony may replace arsenic for the

fabrication of ultrashallow *n*-type layers for future generations of complementary metal oxide semiconductor devices ref Erik Collarts IIT paper.^{4(a)} In this article the effects of changing the tilt angle on the substitutional fraction and the electrical activation of the dopant antimony will be presented.

EXPERIMENT

The first batch of 200 mm Si wafers were implanted with 70 keV $5 \times 10^{14} \text{ Sb}^+ \text{ cm}^{-2}$, at RT with tilt angles of 0° , 15° , 30° , 45° , and 60° (all at 0° twist). The second batch was preamorphized using 160 keV Ge^+ with a dose of $1 \times 10^{15} \text{ cm}^{-2}$ prior to the antimony implants which were performed on the SWIFT implanter^{5(a)} manufactured by Applied Materials®. Following implantation the samples were thermally annealed at 700°C for 30 s in order to activate the dopant. The annealing was performed in a Process Product Corporation rapid thermal processor system in a nitrogen ambient. A temperature of 700°C was chosen because the highest activation of antimony has been observed in the temperature range $600\text{--}800^\circ\text{C}$ (Ref. 5(b)) with no measurable diffusion, in contrast to the case for arsenic implants which need higher temperatures, normally in excess of 1000°C . At such high temperatures both antimony and arsenic diffuse rapidly and the peak carrier concentration is lowered

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FIG. 1. SIMS antimony profiles at energy of 70 keV, dose 5×10^{14} ions/cm² for preamorphized samples at different tilt angles.

significantly.^{5(c)} The dynamic secondary ion mass spectroscopy (SIMS) profiles have been carried out by using the magnetic sector CAMECA SC-ultra apparatus. This instrument is equipped with a floating voltage primary column coupled with a secondary extraction system to obtain lower impact energy of primary ion and maintain a good sensitivity.⁶

The analyses have been performed by using a cesium primary beam and monitoring the secondary negative ions $^{28}\text{Si}^{2-}$ and $^{28}\text{Si}^{121}\text{Sb}^{-}$. The impact energy selected for the analyses was 1 keV with an incidence angle of nearly 45°. Under these conditions the decay length has been measured to be 1.8 nm.⁷ The retained dose and the substitutional fraction were determined by Rutherford backscattering and ion channeling using a 1.5 MeV $^4\text{He}^+$ ion beam with two detectors at scattering angles of 166° and 147°. The sheet carrier concentrations were measured using a Bio-Rad HL5500 Hall effect system using the van der Pauw technique.

RESULTS AND DISCUSSION

SIMS profiles have been performed to determine the depth distribution and the retained dose in the as-implanted and annealed samples. In all figures some points have been skipped (every five points) in order to distinguish the different profiles. Figures 1 and 2 show the depth distribution for implants into preamorphized and crystalline silicon with tilt angle from 0° to 60°. Figures 3 and 4 show the depth profiles

FIG. 2. SIMS antimony profiles at energy of 70 keV, dose 5×10^{14} ions/cm² for crystalline samples at different tilt angles.

FIG. 3. SIMS antimony profiles at energy of 70 keV, dose 5×10^{14} ions/cm² for preamorphized samples annealed at 700 °C for 30 s at different tilt angles.

for the same samples after annealing at 700 °C for 30 s. The SWIFT implanter is capable of implanting the same dose regardless of the tilt angle. The wafer can be tilted at arbitrary angles (up to 60°), but the scan is isocentric, that is, the wafer is moved in its plane. Because of this, no cosine terms need to be considered (as the area exposed remains the same, hence, the dose is also the same). The projected range R_p and the straggle σ_p are a function of the tilt angle. If the wafer is tilted at a large angle to the ion beam the effective ion energy normal to the surface is greatly reduced.⁸ The dose (area under the profile) is the same for all the implants; consequently the peak concentration increases because the straggle σ_p decreases with the cosine of the tilt angle (see Table I).

The peak concentration of antimony, for all samples, is higher than the solid solubility of antimony in silicon, 1×10^{20} cm⁻³.⁹ As the tilt angle increases, the peak concentration increases and therefore the number of antimony atoms in excess of the solid solubility in silicon also increases.

Analysis of the RBS data was carried out using the Datafurnace software.¹⁰

The crystalline sample is also amorphized, by the antimony implant, albeit to a shallower depth than the samples preamorphized with germanium. During annealing epitaxial regrowth occurs and some of the antimony atoms move on to substitutional sites and become electrically active.

FIG. 4. SIMS antimony profiles at energy of 70 keV, dose 5×10^{14} ions/cm² for crystalline samples annealed at 700 °C for 30 s at different tilt angles.

TABLE I. SIMS data for as implanted and annealed (*) samples of *a*-Si and *c*-Si. Sb0, Sb15, Sb30, Sb45, Sb60, refer to the angle of incidence with respect to the normal to the wafer surface. σ_p is the standard deviation of the atomic distribution.

Samples	Dose (at/cm ²)	Peak conc. (at/cm ³)	σ_p (nm)
Sb0 <i>c</i> -Si	5.0×10^{14}	1.63×10^{20}	31
Sb15 <i>c</i> -Si	5.2×10^{14}	1.69×10^{20}	30
Sb30 <i>c</i> -Si	5.1×10^{14}	1.9×10^{20}	28
Sb45 <i>c</i> -Si	5.2×10^{14}	2.06×10^{20}	22
Sb60 <i>c</i> -Si	4.7×10^{14}	2.21×10^{20}	18
Sb0 <i>a</i> -Si	5.0×10^{14}	1.66×10^{20}	33
Sb15 <i>a</i> -Si	5.0×10^{14}	1.75×10^{20}	29
Sb30 <i>a</i> -Si	5.1×10^{14}	1.75×10^{20}	28
Sb45 <i>a</i> -Si	4.9×10^{14}	1.93×10^{20}	26
Sb60 <i>a</i> -Si	4.8×10^{14}	2.12×10^{20}	23
Sb0 <i>c</i> -Si*	5.1×10^{14}	1.75×10^{20}	30
Sb15 <i>c</i> -Si*	5.1×10^{14}	1.78×10^{20}	30
Sb30 <i>c</i> -Si*	5.0×10^{14}	1.83×10^{20}	28
Sb45 <i>c</i> -Si*	5.0×10^{14}	2.08×10^{20}	26
Sb60 <i>c</i> -Si*	4.7×10^{14}	2.15×10^{20}	26
Sb0 <i>a</i> -Si*	5.0×10^{14}	1.66×10^{20}	33
Sb15 <i>a</i> -Si*	5.0×10^{14}	1.77×10^{20}	29
Sb30 <i>a</i> -Si*	5.0×10^{14}	1.86×10^{20}	27
Sb45 <i>a</i> -Si*	4.9×10^{14}	1.97×10^{20}	25
Sb60 <i>a</i> -Si*	4.8×10^{14}	2.15×10^{20}	23

Figure 5 shows the RBS random and channeled spectra for a sample, where the antimony ions were implanted into preamorphized silicon, this sample was annealed at 700 °C for 30 s after implantation. The inset in Fig. 5 shows the antimony and germanium depth distributions in more detail.

The number of counts in the portion of the RBS random spectrum, corresponding to the antimony depth distribution, equates to the total amount of antimony atoms in the sample. The numbers of counts in the same region of the channeled spectrum corresponds to the number of antimony atoms in

FIG. 5. Random and channeled RBS spectra for the sample implanted at 15° tilt with 5×10^{14} Sb⁺ cm⁻² into Ge preamorphized silicon and subsequently annealed at 700 °C for 30 s.

TABLE II. Retained dose and substitutional fraction from RBS measurements at different tilt angles on preamorphized (*a*-Si) and crystalline (*c*-Si) samples annealed at 700 °C for 30 s. The electrical activation from Hall measurements has been reported for comparison and the two sets of data are equal within experimental error.

Sample	Retained dose (atom/cm ²)	Substitutional fraction (%)	Electrical activation (%)
Sb0 <i>a</i> -Si	4.9×10^{14}	96	94
Sb15 <i>a</i> -Si	5.1×10^{14}	94	92
Sb30 <i>a</i> -Si	530×10^{14}	93	90
Sb45 <i>a</i> -Si	4.9×10^{14}	89	87
Sb60 <i>a</i> -Si	4.8×10^{14}	86	85
Sb0 <i>c</i> -Si	5.0×10^{14}	84	82
Sb15 <i>c</i> -Si	5.0×10^{14}	93	90
Sb30 <i>c</i> -Si	4.9×10^{14}	90	87
Sb45 <i>c</i> -Si	4.9×10^{14}	86	83
Sb60 <i>c</i> -Si	4.7×10^{14}	79	77

interstitial sites. From this data the substitutional fraction of antimony atoms (S_f) can be calculated

$$S_f = \left(1 - \frac{C_c}{C_r} \right) \cdot 100\%. \quad (1)$$

C_c is the number of antimony counts in the channeled region of the spectrum and C_r is the number of antimony counts in the random region of the spectrum. Table II shows the total retained dose of antimony and the substitutional fraction as determined by RBS.

In Fig. 5, the negligible channeled yield in the portion of the spectrum corresponding to the germanium depth distribution indicates that the implanted germanium atoms occupy substitutional sites after annealing. Analysis of the spectrum in the region corresponding to antimony shows that 94% of the implanted antimony atoms are in substitutional sites.

The electrical activation of each sample has been defined as the ratio between the sheet carrier concentration from Hall measurements and the total retained dose. Table II also shows the electrical activation, after annealing for all samples.

Comparison of the RBS and electrical data in Table II and Figs. 6 and 7 show a good correlation between the two measurement techniques.

FIG. 6. Substitutional fraction (from RBS) and electrical activation (from Hall) as a function of the tilt angle in preamorphized silicon (*a*-Si).

FIG. 7. Substitutional fraction (from RBS) and electrical activation (from Hall) as a function of the tilt angle in crystalline silicon (*c*-Si).

For all samples the substitutional fraction as determined by RBS is slightly higher than the measured electrical activation. However, because the errors associated with each of the two techniques overlap, we conclude that the two measurements are in agreement, within the experimental uncertainty. For the preamorphized samples the substitutional fraction decreases from 96% to 86% with increasing tilt angle. For the crystalline samples the substitutional fraction increases from 84% to 94%, from 0° to 15°, and then decreases to 79% with increasing tilt angle (to 60°).

This trend is also observed in the electrical characteristics of these samples. All of the peak atomic concentrations recorded in Table I are above the published equilibrium solid solubility limit. Indeed if the percentage electrical activity is taken into account the peak value still remains above this solubility limit. That is, if the percentage electrical activity (Table II) is multiplied by the peak atomic concentration (Table I) a value of $1.6\text{--}1.7 \times 10^{20} \text{ cm}^{-3}$ is obtained, with the exception of the zero tilt implant into crystalline silicon which produces a value of $1.4 \times 10^{20} \text{ cm}^{-3}$. This suggests that the solubility of antimony in silicon under the conditions used for implantation and annealing (700 °C) is $1.6\text{--}1.7 \times 10^{20} \text{ atoms cm}^{-3}$. The electrical activity and the substitutional fraction are lower than expected for the zero degree implant into crystalline silicon (Fig. 7). We found a similar behavior for both arsenic and boron implants and believe that this phenomenon is associated with channeling of the implanted ions, which occurs readily for the zero angle tilt implant and produces a long tail to the atomic distribution. The damage distribution is also modified and in turn, causes a reduction in both the electrical activity and the sub-

stitutional fraction. It is postulated that the excess antimony atoms above our measured solubility are accommodated in the form of clusters or precipitates which are electrically inactive.

CONCLUSION

It has been shown that the substitutional fraction is a function of the implant tilt angle and can be correlated with the fraction of electrically activated antimony atoms. The maximum activation of antimony (9%) is observed at 0° tilt for implants into amorphous silicon. In crystalline silicon the maximum activation (90%) is observed at 15° tilt. For all tilt angles the electrical activation in preamorphized silicon was greater than for the same implant into crystalline silicon. Our data suggest that the solubility limit of antimony in silicon at 700 °C is about $1.6\text{--}1.7 \times 10^{20} \text{ cm}^{-3}$.

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- ¹G. Carter and W. A. Grant, *Ion Implantation of Semiconductor* (E. Arnold, Ltd., 1976).
- ²T. Nishimura, Proceedings of the 2000 International Conference on Ion Implantation Technology 2000, pp. 20–24.
- ³T. Hori, Tech. Dig. - Int. Electron Devices Meet. **1994**, 75.
- ⁴W. K. Chu, J. W. Mayer, and M.-A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978). (a) Erik Collarts IIT paper.
- ⁵(a) G. Claudio, G. Boudreault, C. Jeynes, R. Low, and B. J. Sealy, International Conference on Ion Implantation Technology IIT 2002 (to be published). (b) Tahlals published/unpublished work ask B.J.S. for details. (c) T. Alzanki *et al.*
- ⁶E. De Chambost, B. Boyer, B. Rasser, and M. Schuhmacher, in *Secondary Ion Mass Spectrometry SIMS XII*, SIMS XII Conference Proceedings, edited by A. Benninghoven, P. Bertrand, H.-N. Migeon, and H. W. Werner (Wiley, Chichester, 2000), pp. 533–536.
- ⁷M. Anderle, M. Barozzi, M. Bersani, D. Giubertoni, P. Lazzeri, Proceedings of the 2003 International Conference on Characterization and Metrology for ULSI Technology, Austin, Texas, 2003 (to be published).
- ⁸L. De Cata, J. S. Williams, and H. B. Harrison, Nucl. Instrum. Methods Phys. Res. B **4**, 368 (1984).
- ⁹D. Nobili, R. Angelucci, A. Armigliato, E. Landi, and D. Solumi, J. Electrochem. Soc. **136**, 1142 (1989).
- ¹⁰N. P. Barradas, C. Jeynes, and R. P. Webb, Appl. Phys. Lett. **71**, 291 (1997).