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Positron Annihilation Study of P Implanted Si

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DEC 23 1992 P. Asoka-Kumar,⁽¹⁾ P. Sferlazzo,⁽²⁾ H.L. Au,⁽¹⁾ and K.G.

Lynn⁽¹⁾

⁽¹⁾ Brookhaven National Laboratory, Upton, New York, 11973

⁽²⁾ Eaton Corporation, SED Division, Beverly, Ma 01915

High-energy ion implantation (above 200 keV) is now commonly used in a variety of VLSI processes. The high energy required for these implants is often achieved by implanting multiply charged ions, which inevitably brings in the problem of low-energy ion contamination. The low-energy contamination is difficult to diagnose and detect. Positron annihilation spectroscopy is used to examine the defect distributions in these high energy implants with varying degrees of contamination.

Introduction

In ion implantation the kinetic energy of the implanted ions is dissipated through collisions with the lattice atoms. Besides introducing dopants at various depths, ion implantation creates large amount of defects in the host wafer, in particular vacancies, with higher doses leading to the amorphization of the wafer. Crystallinity is usually recovered through solid phase epitaxial regrowth. Positron annihilation spectroscopy (PAS) is a non-destructive technique with high sensitivity for open-volume-type defects, such as vacancies, voids, and dislocations.[1] PAS of overlayers, interfaces, and buried regions of semiconductors has seen rapid growth in the past

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few years.[2] In this paper we report PAS of damages in P implanted Si.

High energy ion implantation (> 200 keV) is now increasingly used in a variety of VLSI processes, including well and retrograde-well implants, and in the formation of buried layers (conductive and damaged). The high energy required for these implants is often achieved by implanting multiply charged ions. One of the problem associated with the implantation of multiply charged ions, in addition to the lower currents attainable, is the energy contamination from the residual gas scattering in the beam line. As a result there can be significant degradation of ion purity from the same primary chemical element, but with a different charge, mass, or energy. The amount of contamination depends on various source tuning parameters and it is difficult to detect. In particular, dimer break-up in the pre-analysis region can cause considerable fraction of low-energy contamination.[3] PAS has been used in this study to identify low-energy contamination from the break up of the dimer P_2^+ in P^{++} implantations.

Background and Experimental details

The Cz-Si(100) wafers were implanted at 20°C with P^{++} ions and various levels of contamination arising from the break-up of P_2^+ dimers in the pre-analysis region of an Eaton NV20A. All the implantations were done at 7° and there was no significant channeling effects. The pre-analysis terminal voltage was set at 60 keV, so that P^{++} has an energy of 120 keV and P_2^+ an energy of 60 keV before the analysis. In the pre-analysis section (~ 0.5 m long) the P_2^+ breaks up as a result of collisions with residual gas molecules into 30 keV P and P^+ . Typical pressure in the source region was $\sim 1 \times 10^{-5}$ torr. This effect is due to the so called Aston Bands,[4] i.e. $P_2^+ \rightarrow P^+$, leads to fragments which share the same magnetic rigidity, and therefore cannot be resolved by a sector magnet mass spectrometer. After the analysis the beam is accelerated through 70 kV. Hence P^{++} and P^+ are implanted with energies of 260 keV and 100 keV, respectively. Typical dose was 1×10^{13} ions/cm². The intensities of

the two beams are varied between runs. The run parameters for the samples reported in this study are summarized in Table 1.

The fractional contamination of P^+ can be obtained from[3]

$$R = \frac{I(P^+)}{I(P^{++})} 6.6 \times 10^{18} \sigma p l, \quad (1)$$

where R is the fractional contamination, I represent the corresponding intensities, σ is the cross section for the dimer break-up, p is the pressure in torr, and l is the the path length in meters. In the present setup l is ~ 0.5 meters and p is 10^{-5} torr. The cross section is estimated to be 10^{-15} cm². [5] Using the intensities quoted in Table.1 and the above equation, the fractional contamination for the two runs is estimated to be within 2 and 25 %.

From each implantation series one wafer was used as-implanted and the other one was used after an anneal at 1100 °C for positron measurement. The 1100 °C anneal was carried out in a N₂ ambient by rapid thermal processing (RTP). The resistivity of the annealed samples were mapped using a four point probe. The resistivity measurements showed that the dose was uniform (within 1 sigma) across the wafer. The samples were cut into 15 × 15 mm for the positron measurement. The as-implanted samples (i.e. without RTP) were annealed in the positron measurement chamber as described below.

The majority of energetic positrons incident on a solid thermalize rapidly ($\sim 1 - 10$ ps) and annihilate with electrons either from a freely diffusing state or after being trapped at defect sites. In either case two 511 keV γ -rays are produced predominantly. The annihilation γ -rays will appear exactly at 511 keV only when the electron-positron pair is at rest before annihilation. In practice, the γ -rays will be Doppler shifted from the center energy of 511 keV due to the motion of the electrons and positrons prior to the annihilation. Because the thermalized positrons on an

average carry lower momentum compared to the electrons in a solid, the broadening of the annihilation spectra will be dominated by the electron momenta. Hence the γ -ray spectra can be used to sense changes in the vicinity of the annihilation site.

The shape of the annihilation spectra is quantified by defining an S (for shape) parameter. The S -parameter is defined as the ratio of the counts in a small region around the center energy (~ 1.59 keV wide) to the total counts in the annihilation peak. The S -parameter then is a direct measure of the sharpness of the peak. The annihilation spectra will be sharp for annihilations with valence electrons and will be broad for annihilations with core electrons. Hence, the S -parameter will trace changes in the electron environment around the annihilation site. For example, when positrons are annihilating while trapped at open-volume-type defect sites, they are less likely to encounter high momentum core-electrons. Hence, open-volume defects usually produce a high S -parameter compared to defect free material.[1] All the data presented here are normalized to silicon bulk value so that the bulk silicon has a normalized S -parameter of unity.

The positron measurements were performed at Brookhaven National Laboratory using a variable energy positron beam. The details of the positron beam can be found elsewhere.[6] For each incident energy, 1 million annihilation events were recorded in a high purity Ge detector. The S -parameter is evaluated for each of the incident energies, E , resulting in a S -parameter versus energy curve, called a $S - E$ curve. The incident positron energy is related to the mean implantation depth ($\bar{z}$) through a power law given by[1]

$$\bar{z} = AE^n, \quad (2)$$

where A is a material and energy dependent constant and $n = 1.7$ is an empirically found constant.[7] Using Eq. 2 the positron incident energies can be converted to a

mean penetration or sampling depth.

The isochronal annealing of the samples was carried out in the positron measurement chamber at 10^{-8} torr with a resistively heated tungsten foil kept in contact with the silicon sample backed by a thick (~ 1.5 mm) tungsten plate. The temperature of the sample was measured with a thermocouple, kept in contact to the front surface of the specimen. The thermocouple was calibrated with a single color infrared pyrometer for temperatures above 500 °C. The temperature measurements reported here are estimated to be within ± 20 °C. The samples were annealed each time for 15 minutes and all the measurements were performed after a slow cool down to room temperature (typically 1 hour).

All samples were measured as-implanted and after the removal of the native oxide layer. Recently, it was shown that the removal of the native oxide layer greatly increases the sensitivity of the positron measurement by removing an additional parameter deciding the $S - E$ behaviour near the surface.[8] The native oxide layer is removed by dipping the sample in 1:20 48% HF:H₂O for 10 s, followed by 10 s in H₂O, and repeating the procedure three times. The pump down to 10^{-3} torr was achieved in less than 15 minutes after this cleaning.

Results and Discussion

Fig. 1 shows $S - E$ results from a specimen with P⁺ contamination of 2%. The two data sets correspond to measurements before and after the removal of the surface oxide layer by etching. On the top axis are shown corresponding mean implantation depths. From TRIM calculations the projected range of 100 keV and 260 keV phosphorus ions in Si are 133 ± 44 and 333 ± 85 nm, respectively. A visual inspection of the positron data shows that the depth of the defective regions are in rough agreement with the TRIM estimate. A more precise estimate for the defect concentrations can be obtained with a fitting procedure.

The fitting is achieved with a numerical program VEPFIT.[9] VEPFIT solves a one-dimensional, steady-state, diffusion-annihilation equation for positrons. The implantation profile is approximated with a derivative-gaussian. The fitting procedure can vary defective layer boundary and the effective diffusion length of positrons in the defective layer. The effective diffusion length, $L_{eff}(z)$, modified by the presence of defects, is related to the defect concentration, $c(z)$, by

$$k_t c(z) = \left[\left(\frac{L_+}{L_{eff}} \right)^2 - 1 \right] \lambda_b. \quad (3)$$

The annihilation rate of positrons in defect free silicon is $\lambda_b = 4.5 \times 10^9/\text{s}$. [10] The specific trapping rates for defects such as mono- and divacancies in Si are 10^{15}s^{-1} . [11] A short effective diffusion length indicates more defects and vice versa. For example, from the results of as implanted samples in Fig. 1, we can conclude that the near surface region ($\leq 5\text{keV}$) is very defective. This is as follows. For a given region, if the S -parameter at the boundaries are different (in our case the S -value at the surface and the defective layer), the slope of the $S - E$ curve is a measure of the effective diffusion length of the positron.

A best fit is obtained using a defect profile generated by TRIM. The defect profile obtained from TRIM calculations are subdivided into 100 nm interval as shown in Fig. 2. With the use of this defect distribution, the data shown in Fig. 1 can be fitted with reasonable agreement, provided an extra electric field directed into the substrate is added to the end of the TRIM defect profile range. These fitted curves are shown as solid lines in Fig. 3, with and without this electric field. As is clear from the broken-line fit in Fig. 3, the electric field is required to obtain an optimum result. The electric field effects are known from earlier studies on defective silicon.[1] The difference between the fitted results for the HF etched and the as implanted specimens were from the surface contribution. Usually a native oxide layer has a S -value well

below the bulk Si S -value.[8]

A similar set of curves were obtained for wafers with 25 % contamination. These results are shown in Fig. 4. There are no significant differences between data sets shown in Fig. 1 and 4. The solid lines through the data points are again obtained with TRIM defect profile and an additional electric field at the end of TRIM profile.

In Fig. 5 we show the annealing studies for the samples with 2 % contamination. Data correspond to 500, 600, 700, and 1100 °C anneal. The 1100 °C anneal was done by RTP at Eaton corporation. All other anneals were performed in the positron measurement chamber as described in the previous section. Several features are evident in these data sets. For anneals at ≤ 500 °C, the $S - E$ curve was nearly the same as the pre-annealed one. Starting at 600 °C the S -values for the top defective region start to decrease.

At 700 °C the S -parameter drops below the bulk value. A shallow dip develops in the $S - E$ curve at around 100 nm which coincides with the range of P^+ . A dip in S -value below the bulk crystalline value is difficult to interpret. Such a low S -value is typically associated with vacancy clusters decorated with oxygen. SiO_2 -Si and SIMOX results have shown such a low S -value for defects associated with oxygen.[12][13] The most likely source of the oxygen is the Cz-Si itself. However, one cannot rule out phosphorus-vacancy clusters. A measurement with a float zone silicon wafer and a Cz-Si with different oxygen content can differentiate between these scenarios. A similar drop in S -value during anneal also was observed in Si-implanted Cz-Si.[14] Girka et.al., using a positron life-time technique, have shown that both the oxygen and phosphorus impurities influence the annealing of defects generated by proton implantation.[15] Cho et.al. used positron life-time and angular correlation of annihilation radiation to show the recovery stages of defects generated in proton irradiated wafers of varying oxygen content.[16] A sharp drop in S -parameter was

observed at 600 °C. However, they did not observe any significant difference between samples with oxygen contents of $2.2 \times 10^{17} \text{ cm}^{-3}$ and $8.8 \times 10^{17} \text{ cm}^{-3}$.

A 1100 °C RTP produced nearly a perfect Si crystal as indicated by the nearly flat $S - E$ data (see Fig. 5). A flat $S - E$ curve is indicative of defect free silicon without the native oxide layer.[8] A small increase of S towards the surface may be due to residual defects left in these regions. We have seen similar trends in all five of the RTP specimens (with different P^+/P^{++} ratios). However, the present measurements cannot identify any difference between these residual defects. The increase of S -parameter from 700 °C to 1100 °C is probably caused by the break-up of the vacancy clusters responsible for the low S -value. This will be consistent with a scenario where oxygen escapes the specimen as volatile SiO compound during the anneal. A similar set of curves were also obtained for a specimen with 25 % P^+ contamination. It is also worth noting that the 1100 °C anneal was carried out in N_2 ambient and a high vacuum anneal to 1100 °C may not be identical to the RTP in N_2 .

The comparison of 600 °C anneal results of 2 % and 25 % contaminated specimens is shown in Fig. 6. There are clear differences between these samples in the top 100 nm layer. For the sample with higher contamination, a higher S -value is obtained, consistent with a higher defect concentration. Since the S -parameter has saturated after implantation the difference between them are not visible from the as implanted samples. However, as the defects start to anneal out, the fraction of defects remaining can still trap positrons. It is also worth noting that the difference tends to disappear after $\sim 100 \text{ nm}$, which is close to the P^+ range obtained from the TRIM.

PAS is extremely sensitive to defect concentrations as indicated by eq. (3). In our dose range, the positron signal has saturated, i.e. all of the positrons are trapped and are annihilating at defect sites. Hence, the defects generated by low-energy

contamination will not greatly alter the S -parameter at high doses. The effect of low-energy contamination would probably be greatly enhanced in implantations with much lower doses.

Conclusion

In conclusion, our preliminary studies show that positron annihilation spectroscopy can be used as a sensitive probe for studying defect interactions in ion implanted Si. We have examined Si wafers with P^{++} ions contaminated with various degree of P^+ . The annealing study reveals that the PAS is sensitive to the defects generated by the low-energy contamination. The annealing stages observed at 600 °C need further study. We are in the process of further studying these effects, and measuring their dependence on dose.

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TABLES

TABLE I. Summary of ion implantation parameters used for the present study. The P^+ and P^{++} implantation energies were 100 keV and 260 keV, respectively. The intensities are denoted as I . The total dose for all implantations were 1×10^{13} ions/cm².

$I(P^{++})$	$I(P^+)$	Resistivity (Ohm/sq)
0.5	0.4	843
0.5	0.4	894
3.7	0.9	800
1.3	1.3	813
0.5	4.3	770

FIGURE CAPTIONS

1. The $S - E$ data for a Cz-Si sample irradiated by 260 keV- P^{++} with a 2 % contamination of 100 keV- P^+ . The measurements are performed before and after the removal of the native oxide layer and show the influence of this surface layer on the positron measurement.
2. The defect profile used in the fitting procedure. The profile is obtained from TRIM calculations and is approximated into 100 nm wide bins. The solid line correspond to 25 % contamination and the broken line correspond to 2 % contamination of P^+ . In both cases the total dose (i.e. P^{++} and P^+) is taken as the implanted dose (10^{13} ions/cm²).
3. Fitted $S - E$ curves for the samples with 25 % P^+ contaminations. The solid line is obtained by introducing an electric field of 2400 V/cm directed into the bulk silicon from the defective region. The broken line does not have the electric field and is otherwise identical to the solid curve. The fitted curves for the samples with and without the native oxide layers differ only in the surface $S-$ values and a field directed towards the surface (500 V/cm).
4. Fitted $S - E$ curve for samples with 2 % contaminations. The curves are similar to the results shown in Fig. 3.
5. Annealing results of a sample containing 2 % contaminations. The 1100 °C anneal is by RTP in a N_2 ambient. The rest of the anneal is at 10^{-8} torr and is achieved by a heated backing foil. All measurements were performed after etching the native oxide layer in aqueous HF solution. The specimen showed little change upto 500 °C. The decrease at 700 °C is due to vacancy complexes,

either decorated with oxygen or phosphorus. At 1100 °C the specimen recovers the bulk silicon behaviour. - -

6. The $S - E$ data taken after a 600 °C vacuum anneal for samples with different P^+ contaminations. There is a clear difference in the surface region and indicates presence of more defects near the surface of a specimen with higher contamination.

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