Total dose measurement for ion implantation using laser ablation ICP-MS†

JAAS
Interlaboratory Note

Fuhe Li,[a] Marjorie K. Balazs[a] and Raymond Pong[b]

[a]*Balazs Analytical Laboratory, 252 Humboldt Court, Sunnyvale, CA 94089-1315, USA*
[b]*Implant Center, 2121 Zanker Road, San Jose, CA 95131, USA*

Received 6th March 2000, Accepted 28th July 2000
Published on the Web 23rd August 2000

Laser ablation coupled with a quadrupole based ICP-MS (LA-ICP-MS) has been used for quantitative analysis of the total dopant dose implanted in crystalline silicon wafers. Four commonly used dopant ions in the semiconductor industry, namely $^{11}B^+$, $^{75}As^+$, $^{121}Sb^+$ and $^{31}P^+$, were studied in this work. The penetration depths and vertical profiles of these implanted ions in silicon were simulated using 'stopping and range of ions in matter' (SRIM) and utilized to help select the laser sampling parameters. The ICP-MS conditions were optimized to obtain the best signal-to-noise (S/N) and signal-to-background (S/B) ratios using the implanted silicon wafers. The linear analytical calibration curves have been constructed from the standardized wafers with both <100> and <111> crystal orientations. Multiple prime wafers with known dopant ion concentrations implanted at 80 KeV have been used to assess the analytical precision and accuracy of the technique. It is our hope that this method can eventually be utilized to calibrate ion implanters in different fabrications and correlate the total dose levels employed in different fabrication processes for very large scale integration (VLSI) and ultra-large scale integration (ULSI) devices.

With the rapid increase in the complexity and functionality of semiconductor integrated circuits (IC), ion implantation has essentially become the dominant doping technique, particularly in the fabrication of sophisticated bipolar-CMOS devices and in the formation of shallow junctions.[1] Ion implantation delivers well-controlled vertical concentration profiles in the CMOS by directly injecting ions into crystalline silicon. This process can also form highly-doped and defect-free shallow junctions needed for fabrication of advanced integrated circuit (IC) devices.[1] As the design rules of the device shrink into the $\leqslant 0.18$ μm regime, the control of the total dopant dose (the total number of implanted ions per unit wafer area) becomes critical.

The total dopant dose is currently estimated by sheet resistance, capacitance–voltage (C–V) and thermal wave.[2] Due to their indirect measurement nature, the analytical accuracy of these methods is significantly affected by the presence of other ions in the crystalline silicon and the different annealing conditions. Secondary ion mass spectrometry (SIMS) has been extensively used as an excellent depth-profiling tool in the semiconductor industry. However, establishing the accuracy of the total dose measurement is difficult, mainly due to the matrix effect on the yield of the ions directly formed by the ion bombardment. In our laboratory, we have been developing quantitative methods not for depth profiling but for total dose measurement, to help monitor and control the ion implantation process. One of the approaches we have taken is to employ laser ablation sampling coupled with inductively coupled plasma mass spectrometry (LA-ICP-MS). Unlike SIMS analysis, the sampling process of this arrangement is separated from the ionization process. The laser ablation is solely responsible for sampling. The ions formed due to the high power, pulsed laser radiation were not measured. The total ablated materials, including ions, atomic vapor and micro particles, are transported from the laser ablation chamber to a "hot" ICP for re-ionization followed by mass spectrometric measurement. Because the steady-state ICP plasma is a very efficient ionization source, the ion yield that results from the re-ionization in the ICP is perhaps more consistent for a known amount of analyte, and more representative of the ions implanted in the wafer bulk, with less matrix effect. To our knowledge, LA-ICP-MS has not been applied in the ion implantation area prior to this publication.

†Presented at the 2000 Winter Conference on Plasma Spectrochemistry, Fort Lauderdale, FL, USA, January 10–15, 2000.

Experiment

A CETAC Model LSX-100 laser ablation system and a Perkin Elmer Model Elan 6000 ICP mass spectrometer were used in this work. During the course of the development, we studied and optimized the laser operating parameters and ICP-MS conditions for this particular application. The Nd : YAG Q-switched laser with a pulse length of 8 ns was operated at 266 nm in repetitively pulsed mode. The sample positioning and laser focuses were done by a computer-controlled X-Y-Z translation stage, where the laser ablation chamber is mounted. The visual identification of the sample area of interest and laser focusing on the Si wafer surface were provided by a color CCD camera microscopic viewing system. The laser sampling was performed by scanning across the wafer surface in a rastering fashion with several thousand pulses used for each sample area. The generated microparticles, ions and atomic vapor were mixed in the laser ablation chamber and then directly introduced into the ICP by an argon carrier gas. To minimize the possible analyte loss and enable quantitative sample transportation, the outlet of the laser ablation chamber was closely interfaced with the ICP torch inlet of the mass spectrometer. The operating parameters for the ICP-MS included a forward power of 1.35 kW, a reflected power of <5 W, an argon coolant flow rate of 16 L min^{-1}, an auxiliary flow rate of 0.7 L min^{-1}, and a nebulizer gas flow rate of 1.0 L min^{-1}. The ICP-MS signals were acquired in a time-resolved mode and integrated as a function of time. The wafers used for this work were typically implanted at 80 keV on an

DOI: 10.1039/b001796p

Eaton Model NV10 ion implanter with a full ring clamp disk through a 7 degree tilt and 45 degree twist. The implanted wafers were then annealed at 1100 °C for 10 s.

Results and discussion

In order to select the proper laser output parameters and to obtain a representative sampling in depth, it is essential to understand how deep the implanted ions penetrate inside the crystalline silicon with different ion energies under specific implantation conditions, because the dose varies with the penetration depth. Typically the peak concentration is below the surface and varies depending upon the ion energy and the type of ion. Besides using SIMS to obtain a depth profile for the implanted ions, the industry quite often uses the projected range tables generated from 'the stopping and range of ions in matter' (SRIM) to calculate or predict the depth distribution of implanted ions in silicon.[3] The SRIM is a group of programs written by Ziegler and colleagues at IBM which uses a quantum mechanical treatment of ion–atom collisions and assumes the ions implanted into the silicon substrate obey a Gaussian distribution.[3] In most cases, the simulated data correlate very well with SIMS results. Fig. 1 shows the simulated depth profiles of $^{75}As^+$, $^{31}P^+$ and $^{11}B^+$ implanted ions at 80 KeV. It can be seen that the penetration depth of these ions in the silicon substrate is typically less than 1 μm, with $^{11}B^+$ penetrating deepest at around 0.8 μm. With this depth information, the laser output energy and focus were adjusted accordingly so that the laser sampling depth was greater than 1 μm. With a $\geqslant$1 μm laser sampling depth, the implanted $^{11}B^+$, $^{31}P^+$, $^{75}As^+$ and $^{121}Sb^+$ ions can be completely sampled. Additionally, a rastering technique with repetitive pulsing was utilized to ensure that representative spatial sampling and good analytical precision were obtained. Although the greater sampling area generates better analytical precision, a sampling area of 0.5 cm^2 was typically chosen for this work to keep the analysis time practical. This sampling area was also used to calculate the total number of implanted ions per unit area, which is the total dopant dose.

Fig. 2 shows a continuous steady-state and time-resolved ICP-MS signal profile for the $^{11}B^+$ dopant ion. This signal profile was generated by rastering across a boron-doped wafer surface with a dose concentration of approximately 2.0×10^{15} ions cm^{-2}. As shown in the figure, the signal begins at approximately 7 s after the laser initiation and increases dramatically, reaching the maximum at approximately 80 s. The signal then levels off to form a plateau while the laser continuously rasters across the wafer surface. After the laser is switched off, the signal quickly decays to baseline within 15 s. No long tailing was observed.

The signal profile shown in Fig. 2 suggests that, after optimization of the laser parameters and ICP-MS conditions, the atomic vapor and microparticles generated inside the laser chamber can be rapidly and efficiently transferred to the ICP for analysis.[4] The laser ablation chamber, transfer line and ICP touch injector appeared to be clean even after more than 30 sample runs. Memory effect was minimal between subsequent sample runs.[4] Compared to a single pulsed laser, the continuous ICP-MS response obtained by a repetitively pulsed laser coupled with the rastering technique provides better sampling reproducibility and analytical precision, which are critically needed for performing quantitative analysis by LA-ICP-MS.[5]

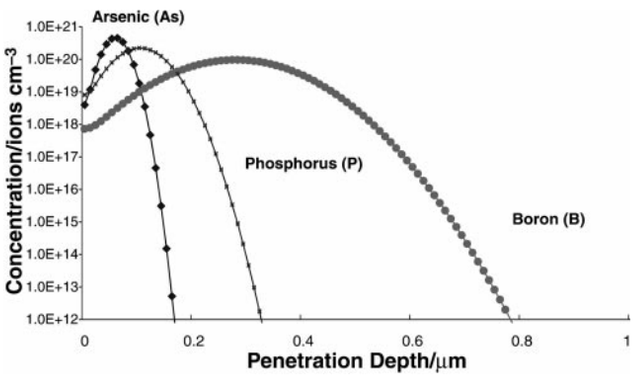

Fig. 1 Simulated concentration *versus* penetration depth.

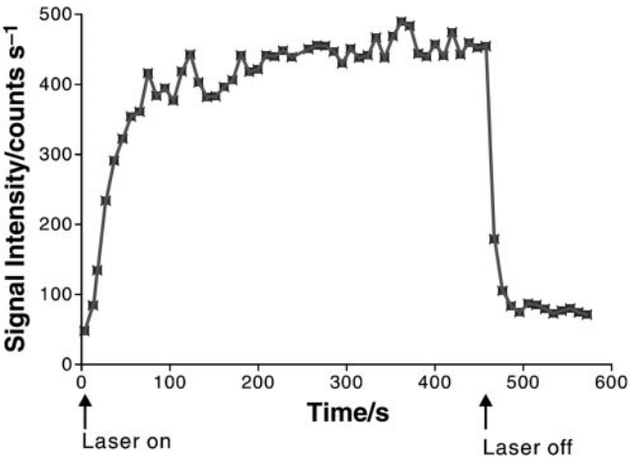

Fig. 2 Time-resolved $^{11}B^+$ signal profile obtained with a boron-doped Si wafer.

Fig. 3 shows the $^{11}B^+$ calibration curve constructed from the wafer standards with <100> and <111> crystal orientations. The calibration curve obtained shows an acceptable linearity with a correlation coefficient of 0.9998, suggesting that the laser sampling and sample transportation from the LA cell to the ICP are quantitative. The laser sampling process using the rastering technique was independent of the crystal orientations of the silicon wafers used. The linear calibration curve obtained also suggests that the ablated materials were consistently transported from the laser ablation chamber to the ICP and vaporized, atomized and ionized.[4] Calibration curves were also constructed for other commonly used dopant ions such as $^{75}As^+$, $^{121}Sb^+$ and $^{31}P^+$. Similar linearity was obtained with correlation coefficients of 0.995 or better.

Multiple silicon wafers implanted at 80 KeV with the predicted dose of 5.0×10^{14}–2.0×10^{15} ions cm^{-2} were analyzed to assess the analytical precision and accuracy of LA-ICP-MS for dose measurement. RSDs for three replicates were found to be in the range of 5 to 10%, depending upon the dopant ions. The initial quantitative results obtained for $^{11}B^+$ ion are shown

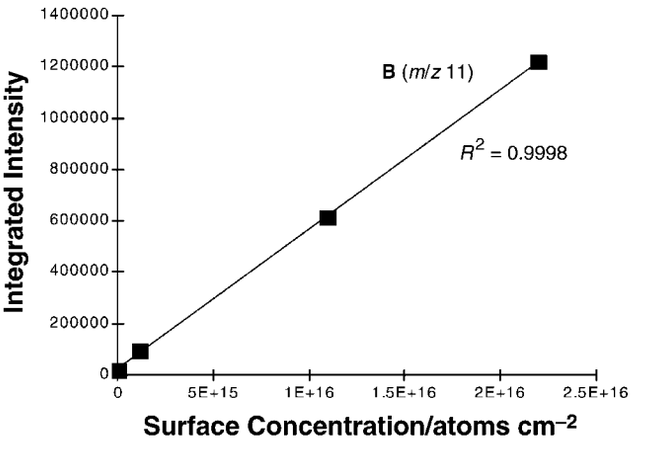

Fig. 3 Calibration plot for boron implant constructed from wafer standards.

Table 1 Quantitative analysis of dose of $^{11}B^+$ implanted into silicon by LA-ICP-MS

Ion	Predicted/ ions cm^{-2}	Found/ ions cm^{-2}	s ($n=3$)/ ions cm^{-2}	RSD (%)
$^{11}B^+$	5×10^{14}	6.6×10^{14}	$\pm0.3\times10^{14}$	4.5
$^{11}B^+$	2×10^{15}	2.1×10^{15}	$\pm0.2\times10^{15}$	9.5

in Table 1. The predicted dose was obtained using SRIM and measured with the sheet resistance technique.

It can be seen that the results obtained by LA-ICP-MS were in the predicted dose ranges. No significant matrix effect was observed. These results may be due to the fact that the standard wafers used for constructing calibration curves and sample wafers were of similar or constant composition.[4] Additionally all of the wafers used were prime wafers with consistent low surface roughness. Knowing that the laser sampling depends not only on the laser parameters but also on the optical, electronic and thermodynamic properties of the sample surface,[6] the amount of material removed by the repetitively pulsed laser ablation was also investigated. The wafer sections were weighed on an ultra micro-balance before and after the laser ablation. It was found that the total amount of material removed by the repetitively pulsed laser was consistent, at a fixed laser sampling frequency and rastering time. We are currently evaluating the analytical precision and accuracy of LA-ICP-MS for measurement of $^{75}As^+$, $^{121}Sb^+$ and $^{31}P^+$ ions and have been conducting more experiments to improve the overall analytical precision. It is our hope that this method can eventually be utilized as an industrial standard to calibrate ion implanters in different fabrications and to correlate the total dose levels used in different IC fabrication processes. It may also provide an independent method for comparison with SIMS total dose data.

Acknowledgement

The authors would like to thank Dr. Mark J. Camenzind for his valuable comments concerning this work.

References

1 D. W. Duff and L. M. Rubin, *Solid State Technol.*, 1998, **41**(6), 83.
2 M. I. Current, *Basics of Ion Implantation for Integrated Circuit Manufacturing*, Greater Silicon Valley Ion Implant Users Group, 1994, ch. 3, pp. 1–10.
3 J. F. Ziegler, J. P. Briersack and U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon Press, New York, 1996.
4 A. Montaser, *Inductively Coupled Plasma Mass Spectrometry*, Wiley, New York, 1998, ch. 3, pp. 194–220.
5 R. E. Russo, *Appl. Spectrosc.*, 1995, **49**(9), 14A.
6 A. J. Campbell and M. Humayun, *Anal. Chem.*, 1999, **71**(5), 939.