Analytical Techniques for Measuring Contamination Introduced During Ion Implantation

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Abstract - Contamination introduced during ion implantation, including transition metals, mobile ions, carbon and particulates can be deposited on the surface of the Si wafer or can be co-implanted to depths of 100s of angstroms. A host of tools are used today to measure these contaminants; amongst these are magnetic sector SIMS (Secondary Ion Mass Spectrometry), quadrupole SIMS, (TOF) Time of Flight SIMS, surface SIMS or "O" (Oxygen) - Leak SIMS, Total Reflection X-Ray Fluorescence (TXRF), Vapour Phase Decomposition (VPD) - TXRF, VPD - AA (Atomic Absorption) and Minority Carrier LifeTime (MCLT).

In this paper, some of the advantages and shortfalls of using the above techniques will be considered for the measurement of heavy metals, mobile ions, Aluminium and cross - contamination of dopants introduced during ion implantation.

Introduction

As silicon device geometry continue to shrink, process technology becomes more complex, product cycles get shorter, and the need for higher yield figures become essential. To keep up with these demands, process equipment such as ion implanters have to become ever cleaner through improved design. This in turn requires the need for improving the performance of analytical tools and measurement techniques for evaluating the lower levels of contamination in implanted silicon wafers. The analysis of trace levels of contaminants require the correct choice of measurement technique, and careful experimental design and data analysis to eliminate random and systematic errors.

In this paper we shall consider some of the advantages and disadvantages of using magnetic sector SIMS (Secondary Ion Mass Spectrometry), quadrupole SIMS, TOF (Time of Flight) SIMS, Surface or "O"(Oxygen)-Leak SIMS, TXRF (Total X-Ray Reflection Fluorescence), VPD (Vapour Phase Decomposition) - TXRF, VPD - AA (Atomic Absorption), MCLT (Minority Carrier Life Time), to evaluate the various impurities introduced during ion implantation. Particular references will be made to recent implant studies.

During an ion implantation process many types of contaminants can be introduced. These can be re-sputtered impurities from the implanter components close to the wafer which are generally introduced on the top 20 to 40 angstrom. Energetic species such as dopant cross contaminants or metals in the beam line can be co-implanted to 1000s of angstroms.

Near Surface Contaminants

A. TXRF

TXRF is a novel surface sensitive technique capable of detecting medium- and high-Z elements (atomic number between 16 (Sulphur) and 92 (Uranium)) at very low levels; detection limits of 10^{10} atoms/cm^2 or better can be achieved for transition metals using the W rotating anode x-ray source of the commercially available Technos TREX 610T. This technique has proved to be particularly effective in the determination of surface elemental densities in the native or chemically grown oxides on polished silicon wafers. A comprehensive description of this technique is given in ASTM Designation: F 1526-94 (1).

In the TXRF technique a well-collimated x-ray beam is made to impinge upon an optically flat substrate in total external reflection geometry (i.e. at an angle less than the critical angle for total external reflection). The incident beam penetrates approximately 30 - 50 angstroms into the silicon surface causing the trace impurities present to fluoresce with a characteristic energy. The spectra of these fluorescent x-rays are obtained by a Si(Li) detector. The surface concentrations of the impurities may subsequently be quantified using a proper calibration.

Penka and Hub (2), 1989, reported how the detection limit for particular x-ray series (e.g. K_α) typically increases with decreasing Z. For constant instrumental parameters, the interference-free detection limits vary over two orders of magnitude as a function of the atomic number of the element.

Advantages	Disadvantages
good detection limits for medium and high mass elements	low sensitivity for low mass elements
reliable quantification	no chemical information
multi-elemental analysis	crude lateral resolution
no sample preparation	back of wafers can not be measured with good detection levels
non destructive	

TABLE 1: The advantages and disadvantages of TXRF

Often spurious peaks of Fe Kα and Ni Kα appear in TXRF spectrums (3). The intensity of the spurious peak varies with the changes in incident azimuth angle. The origin of this phenomenon is impurities existing along the path of X-Rays. This phenomenon can influence the accuracy of trace level analysis of impurities. The incident azimuth must be selected so as to be off the Brag condition of the primary beam.

The advantages and disadvantages of the TXRF technique are listed in Table 1.

A typical TXRF spectrum is shown in Figure 1 and the measured impurity concentrations observed are listed in table 2.

B. VPD - TXRF / AA

One method which has provided improvements in the detection limit of TXRF is the incorporation of a pre-concentration step; in this case, vapour phase decomposition (VPD) using HF (hydro fluoric) acid. A description of this technique has been given by Neumann and Eichinger (4), 1991. This pre-concentration of the surface oxide layer (either native or thermal) is followed by an AA measurement of the concentrated droplet or subsequent TXRF measurement on the dried droplet. The sensitivity enhancement of VPD/TXRF can be estimated from the ratio of the total wafer area to the analysis area; improvements of the detection limit in the region of two orders of magnitude may be achieved for a 200 mm wafer.

The collection efficiency of VPD is dependent on the solubility and electrochemical potential of the metallic impurity in the solvent with respect to Si (-0.86V). The recovery rates of some of the elements are shown in table 3.

Iron is one of the most common contaminant which is introduced during processing of VLSI or ULSI devices3.

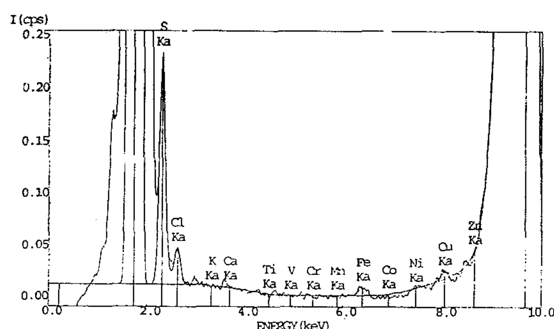

Fig. 1 A typical TXRF spectra from a Phosphorous implanted Si wafer at 50KeV and 5..55 E15 dose.

Table2. Contamination values obtained from the above TXRF measurement of the Phosphorous implanted Si wafer.

Element	Conc. * E10 (atoms/cm2)
S	1784.16
Cl	182.16
Ca	3.76
Fe	3.47
Ni	0.18
Cu	1.92

For the purpose of performing VPD it has been generally been assumed that Fe probably resides as an oxide on the wafer surface; however studies by Pirooz et al.(5) showed that presence of boron, for example in p+ wafers probably form Fe-B pairs and the VPD recovery rate is then significantly lowered. This can be seen clearly in the following data table 4. The SC1 clean which contains dilute HF is not sufficient to remove Fe effectively.

Apart from the issues of ineffective collection efficiencies for some of the elements by the VPD process, there are also several other disadvantages. VPD is a destructive technique, but inherent to it is the possibility of inadvertently adding contamination. It further assumes that the contamination is distributed homogeneously on the wafer. In reality this distribution can vary by one order of magnitude.

C. Surface SIMS or "O"-Leak SIMS

Recently "O"- Leak SIMS (6) has been used as an effective tool for measuring surface contaminants using magnetic sector instruments. Dynamic SIMS proves to be inadequate in the quantification of impurities on the surface of silicon wafers due to the large pre-equilibrium depth of ~200 Å. Within this depth the concentration of oxygen implanted by the primary ion beam increases to an equilibrium value. This means that the yield of the secondary ions are changing continuously making it difficult to provide accurate quantitation. With "O"-Leak SIMS the pre-equilibrium depth disappears and an adequate quantification can be carried out, as shown in figure 2. It can be seen that the residual phosphorous co-implanted during a BF2 implantation measured with dynamic SIMS (Cs primary ion bombardment) gives a value which is almost a factor of 2 lower than the measurement carried out with "O"-Leak SIMS. Due to the higher level of partial oxygen pressure on the sample surface, higher levels of ion yield compared to conventional dynamic SIMS for the same sputter rate can be achieved. In the case of Na and Al for example this results in

TABLE 3: Estimated recovery rates for certain metals by VPD.

Element	Recovery (%)
Cr	60
Ni	72
Cu	<5
Zn	95

Table4. Surface Fe levels on p- and p+ Si wafers after cleaning processes containing HF. The measurements were carried out using TXRF (units of 10^{10} atoms/cm^2)

	SC1	SC1 + H_2SO_4 / HNO_3	SC1 + H_2SO_4 / HNO_3+HF
p- wafer	60	30	10
p+wafer	180	320	80

a detection level of approximately 2E9 atoms / cm2, as shown in figure 3.

Quadrupole SIMS instruments are not suitable for this type of measurement as these are normally designed as UHV (ultra high vacuum) instruments. They also suffer from very low mass resolution capability. This means that it is difficult to separate secondary ions and molecules with the same mass, and at the same time attain good detection levels. However because of the UHV capability carbon contamination introduced on the near surface of the wafer by implantation can be measured more accurately.

"O"-Leak can be used in some TOF SIMS instruments, however quantification is difficult. Due to the fact that these instruments can measure with very high mass resolution, it is ideal for investigating organic and molecular contamination.

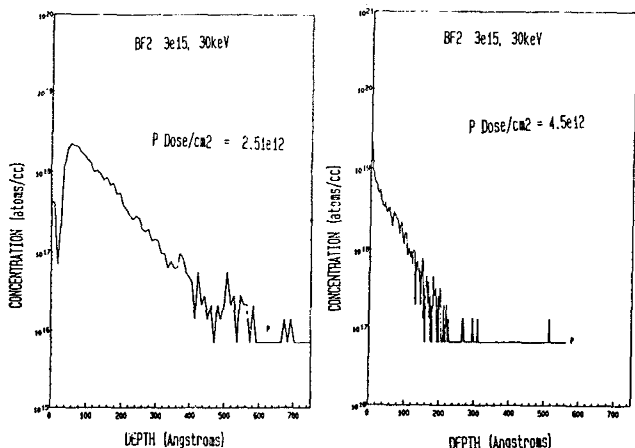

Fig. 2. Residual co-implanted phosphorous measured without "O-Leak" on the left and measured with "O"-Leak on the right. Without "O"- Leak the value measured is approx. a factor of two lower than the real value.

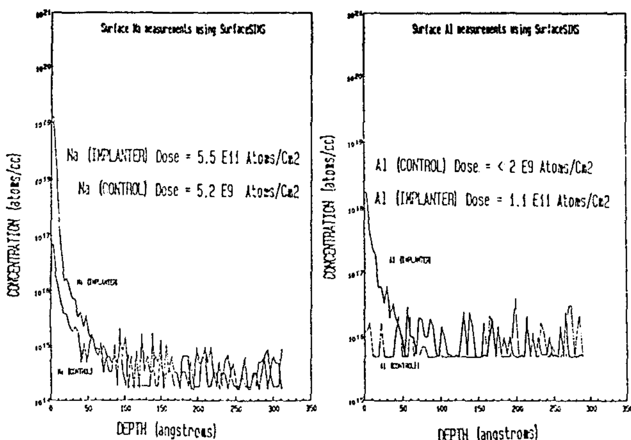

Fig.3. Very good detection levels can be achieved using "O"-Leak for Na and Al contamination introduced during ion implantation. Here ion implanted wafers are compared with control wafers.

Co-Implanted Contamination

During ion implantation cross - contamination of dopants may occur, for example P in a BF2 or As implantation. Impurities such as Al (mass 27), Mo (mass 98) and W (mass 184) can be co-implanted along with B, BF2, As as examples. These types of impurities have been studied extensively by SIMS and are not discussed in detail here. Figure 4 shows a profile of a co-implanted W profile.

MCLT map of metal contaminants

Metallic impurities are not only introduced by sputtering or co-implantation , but also by direct contact. A novel method for investigating metal contaminants is by MCLT mapping. Figure 5 shows a map of an As implanted wafer (1 E15 dose). This wafer was oxidised using a tunnel oxidation process to grow an 80Å oxide after implantation. This thermal process was enough to diffuse the metallic impurities into the wafer, which was subsequently mapped for bulk minority carrier life time. The light areas have lower lifetime values indicating the presence of higher levels of trapping centres caused by metal impurities. It is evident from this picture that the clamps were contaminating the wafer not only by contact, but also by sputtering metals from it.

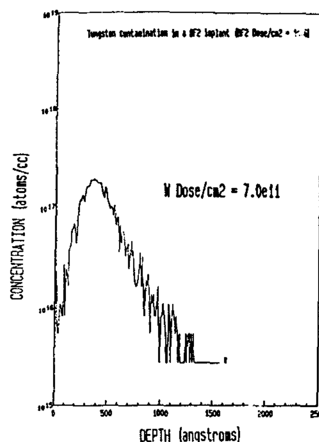

Fig.4. Co-implanted W contamination during BF_2 implantation.

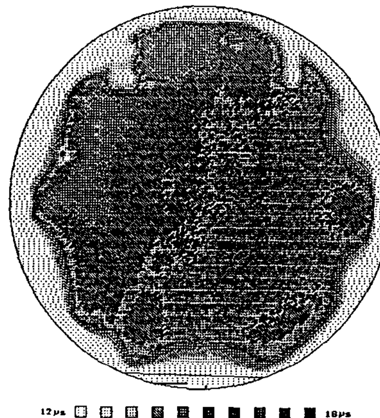

Fig.5. MCLT map of As implanted wafer showing contamination introduced from clamps holding the wafer in the implanter.

References

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