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A Review of Analytical Techniques for Process Control of Contaminants Introduced During Ion Implantation

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Abstract - During the ion implantation process wafers may be contaminated by transition metals, mobile ions, carbon, and organics. These contaminants may arise from (i) deposition onto the surface of the silicon wafer or, (ii) co-implantation to depths of several hundreds of angstroms. A number of analytical tools can be used to characterize these contaminants. The choice of the technique depends on whether a contaminant was introduced non-energetically (contaminant that is located on the surface of the wafer) or energetically (a contaminant that has penetrated into the wafer to some depth). The key parameter to consider when choosing the appropriate analytical tool is its analytical depth of information. Common analytical tools used today to characterize non-energetic contaminants include total reflection X-ray fluorescence (TXRF), SurfaceSIMS, vapor phase decomposition (VPD) with TXRF, time-of-flight SIMS (TOF-SIMS), and minority carrier lifetime (MCLT). In this paper, some of the advantages and shortfalls of using these techniques as a process control tool for ion implantation will be discussed.

I. INTRODUCTION

To keep pace with the increasing demands of the semiconductor industry, process equipment manufacturers must strive to improve throughput and reduce contamination. Reducing contamination is necessary, to improve the product yield of IC devices, as it can be detrimental to the overall performance of the device. In the case of ion implanters, they have to become ever cleaner through improved design. This in turn requires the need to improve the performance of analytical tools and to develop new analytical protocols and measurement techniques for evaluating the lower levels of contamination on implanted silicon wafers. The monitoring 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 consider some of the advantages and disadvantages of using total reflection X-ray fluorescence (TXRF), SurfaceSIMS, vapor phase decomposition (VPD) with TXRF, time-of-flight SIMS (TOF-SIMS), and minority carrier lifetime (MCLT) to evaluate the various impurities that may be introduced during ion implantation processing.

II. SURFACE ANALYTICAL TECHNIQUES

A. *Total Reflection X-ray Fluorescence (TXRF)*

TXRF is well established as a surface sensitive technique. It can detect medium- and high-Z elements (sulphur to uranium) at very low concentration levels. Routine detection limits with a Technos TREX 610T, using the W rotating anode X-ray source, is approximately 10^{10} atoms/cm^2 or better. TXRF has proved to be particularly effective in the determination of surface impurities after ion implantation processing. A comprehensive description of this technique is given in ASTM document, F 1526-94 [1].

In the TXRF technique, a well-collimated X-ray beam impinges 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 the silicon wafer approximately 3-5 nm causing the trace impurities present to fluoresce with a characteristic energy. A Si(Li) detector obtains the spectra of these fluorescent X-rays. The surface concentrations of the impurities may subsequently be quantified using a proper calibration.

Penka and Hub [2], in 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 and is a function of the atomic number of the element.

Often spurious peaks of Fe K_α and Ni K_α appear in TXRF spectra [3]. The intensity of the spurious peak varies with the changes in incident azimuth angle. The origin of this phenomenon is impurity specific and exists 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 I.

TABLE 1

THE ADVANTAGES AND DISADVANTAGES OF TXRF

Advantages	Disadvantages
Survey analysis	10 mm lateral resolution
Full wafers (200mm and 300 mm)	No depth distribution information
Non-destructive	Cannot detect low-Z elements (e.g. Li, Na, K, Al)
Quantitative	Require polished surface

A typical TXRF spectrum is shown in Fig. 1. The corresponding measured impurity concentrations observed by TXRF are listed in Table II.

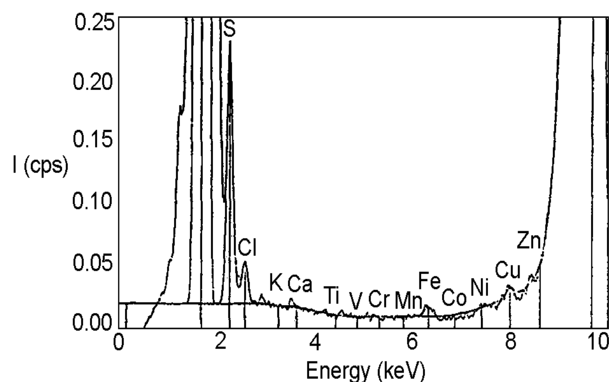

Fig. 1. A typical TXRF spectrum of phosphorus implanted Si wafer at 50 KeV and $5x10^{15}$ at/cm^2 dose.

TABLE II

TXRF CONTAMINATION VALUES OF PHOSPHORUS IMPLANTED WAFER SHOWN IN FIG. 1.

Element	Concentration (x 10^{10} atoms/cm^2)
S	1784.16
Cl	182.16
Ca	3.76
Fe	3.47
Ni	0.18
Cu	1.92

B. SurfaceSIMS

SurfaceSIMS first passed an ASTM consensus ballot for a new document, "Standard test method for measuring surface sodium, aluminum, and potassium on silicon and epi substrates by secondary ion mass spectrometry", in 1995 (ASTM F 1617-95). This document has since been revised to include iron (ASTM F 1617-98). With its demonstrated long-term reproducibility and excellent detection sensitivity, SurfaceSIMS is emerging as an important application of dynamic SIMS for process control of metal contamination introduced during ion implantation. SurfaceSIMS complements TXRF by detecting the low-Z elements, such as Li, Na, K, and Al, and by providing valuable depth distribution of surface impurities. The latter is a key feature to understand the mechanism of inadvertent contamination introduced during the ion implantation process.

SurfaceSIMS was developed to overcome the changing sputter ion yield, associated with the transient region at the near surface, during the initial sputtering process. SurfaceSIMS measurements are made using an oxygen primary ion beam and a magnetic sector mass spectrometer with oxygen flooding. In principle, with oxygen flooding the silicon surface is saturated with adsorbed oxygen and the secondary ions are emitted from a fully oxidized surface. The ion yields are therefore independent of the depth of primary oxygen ion implanted into the sample during the initial sputtering process. As a result, accurate quantification can be made from the sample surface which would otherwise not be possible using conventional SIMS.

The effectiveness of SurfaceSIMS to overcome the low ion yields of the surface transient region is illustrated in Fig. 2, as shown by the constant ion yield for silicon from the sample surface to beyond 150 angstroms.

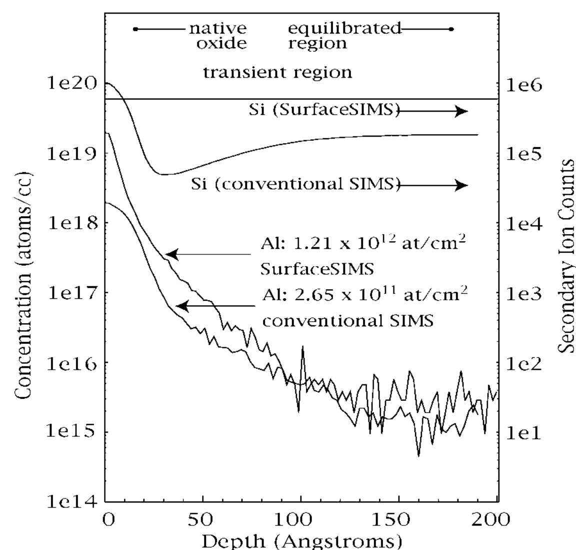

Fig. 2. SurfaceSIMS depth profiles of Si and Al in a boron implanted silicon wafer. The flat silicon profile verifies that the surface transient region is minimised during SurfaceSIMS measurement.

The high mass resolution (HMR) capability of SurfaceSIMS, provided by the magnetic sector mass spectrometer, permits definitive identification of surface contaminants with detection sensitivity [6]. Table III shows the detection limits of selected elements on silicon.

TABLE III

DETECTION LIMITS OF SELECTED ELEMENTS BY SURFACESIMS

Element	Detection Limit ($x\ 10^{10}$ atoms/cm^2)
Li	0.001
Na	0.01
Al	0.05
K	0.01
Ca	0.05
Cr	0.01
Fe	0.08
Ni	1
Cu	1
Mo	0.1
Ta	1
W	0.2

C. Vapor Phase Decomposition - TXRF (VPD-TXRF)

Vapor phase decomposition (VPD) is a "wet chemistry" process. In principle, the VPD process pre-concentrates the surface impurities on the wafer surface using a HF (hydrofluoric acid) droplet. When VPD is used in conjunction with an analytical technique it can provide improvements in detection limit. In the case of TXRF, the HF droplet collects the surface impurities that are residing on the wafer surface. When the droplet dries, the impurities are pre-concentrated into a residue with an area less than the detection area of TXRF. The improvement in TXRF detection sensitivity using VPD therefore increases by the ratio of the total wafer surface area to the TXRF detection area, typically 10 mm. A description of this technique has been given by Neumann and Eichinger [4].

Although VPD has good virtues, there are several caveats to the VPD procedure. The first, is the collection efficiency of VPD. The collection efficiency is dependent on the solubility and electrochemical potential of the metallic impurity in the solvent with respect to silicon (-0.86V). The recovery rates of selected elements are shown in Table IV. Careful recovery experiments are required for accurate quantification.

TABLE IV

ESTIMATED RECOVERY RATES FOR CERTAIN METALS BY VAPOR PHASE DECOMPOSITION

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

Iron is one of the most common contaminant, a component of stainless steel, introduced during processing of VLSI or ULSI devices. For the purpose of performing VPD, it has been generally assumed that the surface Fe chemistry is an oxide when Fe is deposited from a SC1 cleaning solution. With this assumption, the most appropriate chemistry to remove this surface Fe would be dilute HF. However studies by Pirooz, *et al.*, [5] showed that the presence of boron, for example in p+ wafers, probably results in surface Fe forming Fe-B pairs which can affect the VPD recovery rate of surface Fe. Their results of this study are shown in Table V. The important part of the results, for our discussion here, is the poor recovery of surface Fe by the last HF step on the p+ wafer surface compared to the p- wafer surface, a factor of 8x difference. SurfaceSIMS would have obtained the correct surface Fe value with detection limits superior to TXRF.

TABLE V

TXRF SURFACE IRON CONCENTRATION LEVELS REMAINING ON **P-** AND **P+** SILICON WAFERS AFTER CLEANING PROCESS STEPS (UNITS OF 1E10 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

The second problem associated with VPD is the possibility of inadvertently adding contamination from the HF droplet itself. The VPD process requires a HF droplet to be deposited onto the wafer surface; the droplet may be considered a "contaminant" and must be of high purity to not contribute to the wafer surface impurities. Additional problems include the VPD collection, which further assumes that the surface contamination is distributed homogeneously on the wafer. In reality this distribution can vary by one order of magnitude. Particles, if present, are also indiscriminately collected during the VPD process and will lead to incorrect results.

D. Time-of Flight SIMS (TOF-SIMS)

Organic contamination of wafers during the ion implantation process can originate from outgassing of roughing pumps and airborne contamination resulting from implantation into photoresist. Wafer storage boxes are also a source of organics. Although unpolymerized monomers and oligomers outgassed from the box in large quantities, the major species found on the wafer surfaces were from the small quantity of additives in the materials, such as antioxidants, plasticizers, and cross-linking agents. In general, the lower the vapor pressure and the lower the molecular weight the more easily the materials adsorbed onto the wafer surface. The material's polarity also affected its adsorption.

The effect of organic contamination during ion implantation to device performance is not clear, at this time. However, Kasi, *et al*., has showed, by exposing cleaned wafer surfaces to controlled amounts of known organic molecules, that significant amounts ($1x10^{15}$ atoms/cm^2) of hydrocarbon can cause serious degradation of metal-oxide-semiconductor (MOS) devices grown on hydrogen passivated, HF cleaned, (100) Si [8].

TOF-SIMS has several advantages for the measurement of organic contamination. It has very good sensitivity for low levels of contaminants and for low volatility or thermally unstable contaminants that can be difficult to measure by desorption techniques. The high mass resolution of the mass spectrometer can provide unambiguous identification of chemical species. In addition, because the analytical areas are localized and the ions detected are coming from specific, identifiable regions of a wafer, it is possible to compare the levels of contamination from different regions on the same wafer [9].

The most important limitations of TOF-SIMS are related to difficulties with quantification and to the effects of the UHV conditions of the experiment. Quantification is complicated by the large differences in relative ion yields among organic ions. This means that, at present, it is only possible to make relative comparisons of the intensities of a particular species among a series of wafers. The standard UHV conditions of the TOF-SIMS analysis mean that more volatile compounds present on wafers are often removed from the sample before it is measured. Using a cold stage during the analysis [10] can mitigate this problem.

E. Minority Carrier Lifetime (MCLT)

Metallic impurities are not only introduced into the wafer during the ion implantation process by sputtering or co-implantation, but also by direct contact. A novel method for investigating metal contaminants is by MCLT mapping. Fig. 3 shows a map of an As implanted wafer ($1x10^{15}$ atoms/cm^2, 150 keV). This wafer was oxidized using a tunnel oxidation process to grow an 8 nm oxide after ion implantation. This thermal process was sufficient to diffuse the metallic impurities into the wafer, which was subsequently mapped for bulk minority carrier lifetime. 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 map that the clamps were contaminating the wafer not only by contact, but also by sputtering metals from it.

Fig. 3. MCLT map of As implanted wafer showing contamination introduced from clamps securing the wafer in the ion implanter.

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