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Nondestructive Evaluation of Trace Metals and Application to Defect Generation

N.TSUCHIYA, M.TANAKA, M.KAGEYAMA, A.KUBOTA and Y.MATSUSHITA

Semiconductor Group, TOSHIBA Corp.
72, Horikawa-cho, Saiwai-ku, Kawasaki 210, Japan

An innovative nondestructive evaluation method for trace metals on semiconductor wafers by Total Reflection Energy-dispersive X-ray fluorescence (TREX) has been established. It enables distribution analysis and trace analysis as low as 10^{10} atoms/cm^2. The effects of Fe, Ni and Cu concentration analyzed by the TREX on defect generation were made clear by using the same wafer. The nondestructive tracing of the same wafer during treatments proved future utility. Further improvement of sensitivity as low as 10^8 atoms/cm^2 is confirmed by the condensation technique.

1. INTRODUCTION

The evaluation and control technique of trace metals has become a more and more important problem for Si devices, especially for MOS VLSI's, because those metals cause harmful effects on electric characteristics. The trace metals analysis should be nondestructive and convenient, because a quick evaluation of line contamination is required for the device fabrication .

However, the conventional analysis methods of trace metals, such as vapor phase decomposition (VPD)[1] and secondary ion mass spectroscopy (SIMS) do not satisfy the above condition, because they are destructive analysis.

The Total Reflection Energy-dispersive X-ray fluorescence[2] (TREX) is expected to have enough sensitivity for Si wafer surface analysis. However, the lower limit of detection (LLD) is more than 10^{11} atoms/cm^2 [3], which is insufficient for the analysis of VLSI wafers, therefore further improvement of the LLD is required.

In this paper, a newly developed TREX instrument[4] with higher sensitivity and with new function necessary for wafer characterization is introduced. Then its application is shown through the experiments, which proved not only the advantages of the TREX, but also elucidated the behavior of trace metals.

2. A NEW INSTRUMENT

A newly developed instrument was designed for semiconductor wafer analysis, and it has functions to measure the metal distribution on a whole wafer surface in large diameter and to change glancing angles for the distribution analysis along the depth direction[5].

The improvement of the LLD is effectively achieved by monochromatization[6] of a primary X-ray (WL_{β_1}), which enabled the further decrease of background X-ray. Other effective improvements were carried out by adapting a high brightness X-ray tube (9kW rotating anode), the evacuation of sample chamber, and a solid state detector (SSD) with a wider diameter (10mmϕ)

The LLD thus achieved is as low as 10^{10} atoms/cm^2 for trace atoms as Cr, Fe, Ni, Cu

and Zn. A working curve of Cu (Fig.1) reperesents the LLD less than $1x10^{10}$ atoms/cm^2 and good linearity.

3. APPLICATION TO SI WAFERS

3.1 Distribution analysis

The distribution analysis of a full wafer on which Cr is adsorbrd in chemical solution is shown in Fig.2.

3.2 Residual and adsorbed metals

The TREX is advantageous to the other trace element analysis with the collection of impurities by chemical solutions, such as

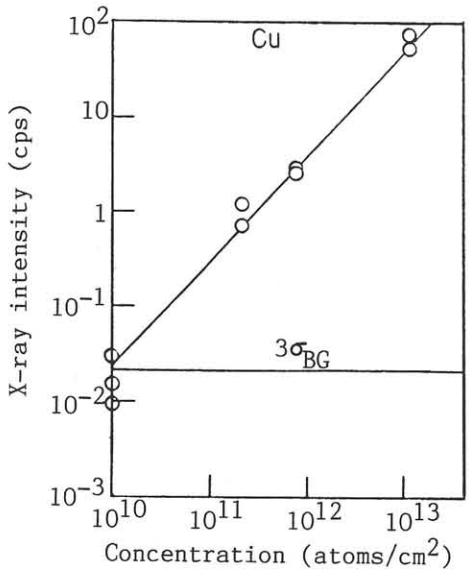

Fig.1 An example of working curve.

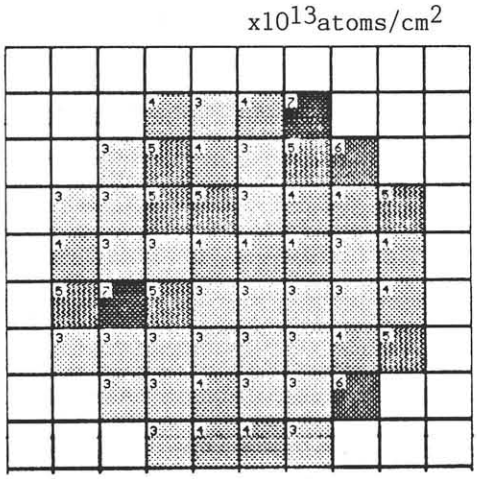

Fig.2 Distribution of intentionally contaminated Cr on 5" Si wafer

VPD. It is easily proved by analyzing an identical wafer before and after the VPD treatment. The obtained value by the VPD is influenced by the solvent of collection drops. Because the collection efficiency depends on the solubility and ionization tendency of metallic impurity in the solvent. On the other hand, since the TREX analyzes the impurities themselves, the obtained value by the TREX is more believable than that of VPD.

The adsorption of transition metals on Si wafers was characterized using the cleaned wafers with hydrophilic and hydrophobic properties. Samples were Czochralski grown (100) n-type and p-type wafers (each type has several Ω-cm in resistivity). Representative five chemical cleaning solutions were adjusted to solute 50ppb Cr, Fe, Ni, Cu and Zn ions, respectively. Then the wafers were dipped into each solution, rinced by deionized water, and dried by a spin drier.

It is clear from Fig.4 that the metal concentration is conspicuously dependent on the kind of solution and initial surface property, not dependent on wafer type. For

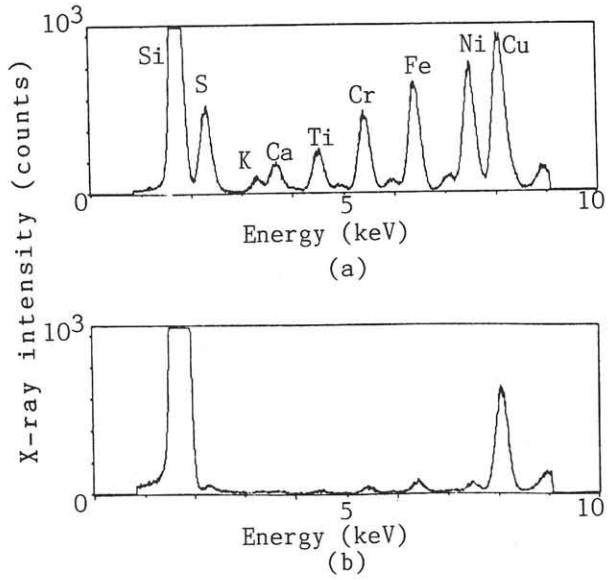

Fig.3 TREX spectra of (a)intentionally contaminated Si wafer and (b) the same wafer after VPD treatment.

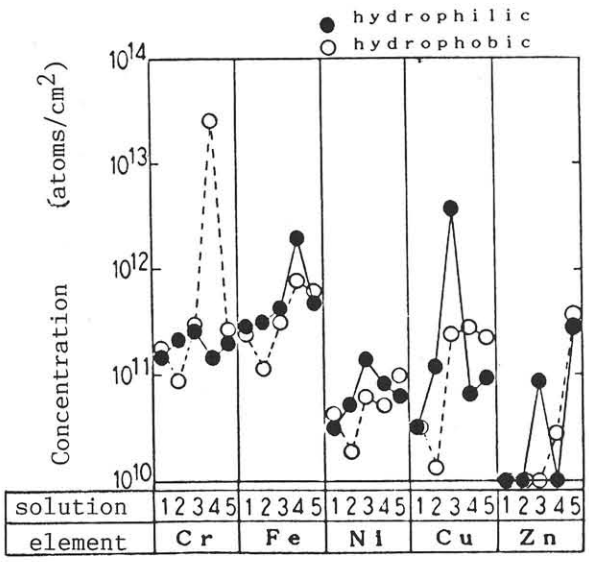

Fig.4 Adsorbed impurity amount analyzed by TREX

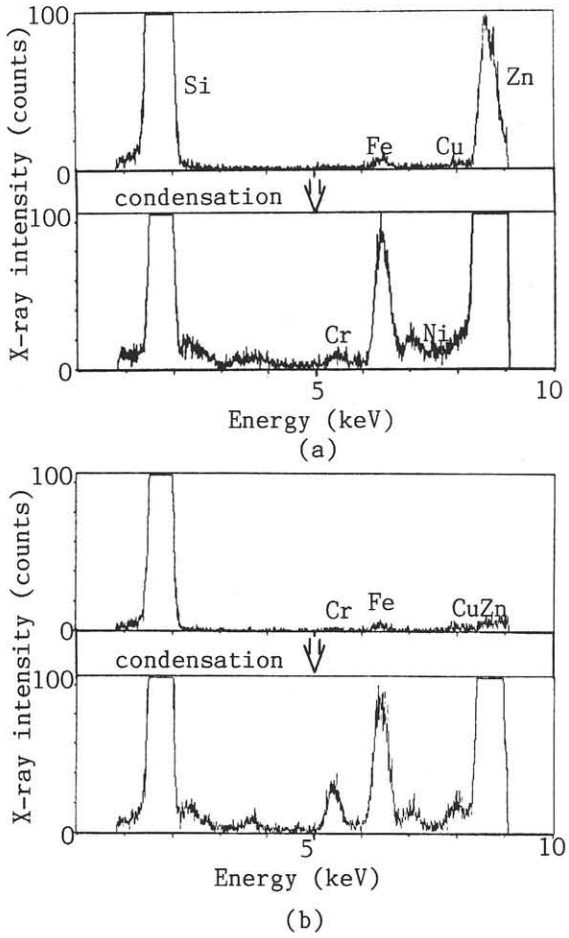

Fig.5 The TREX spectra of wafers from (a) supplier A and (b) supplier B. Upper spectra were measured at the center of as-received wafers. Lower spectra were measured at the condensed area.

example, a large quantity of Cr is adsorbed in solution 4 only in the hydrophobic case.

3.3 Ultratrace analysis on wafer surface

As the TREX detects metals of 10^{10} atoms/cm^2 level for the area approximately 1cm^2, the high sensitivity analysis as low as 10^8-10^9 atoms/cm^2 was invented by analyzing the collected impurities on a whole wafer larger than 5" in diameter, whose area is more than 100 cm^2.

The experiment was carried out as follows: Wafers from two silicon suppliers A and B were analyzed by the TREX (Fig.5). Then surface metals were collected by chemical drop scanning of overall 5" wafer and it was dried on the wafer. After that, the condensed part was analyzed by the TREX (Fig.5).

In these spectra, net intensity ratio (the intensity before the collection devided by that after the collection) is for example, 30 times for Fe, and 40-70 times for Zn. Since the Fe concentration of as-received wafer is several times 10^{10} atoms/cm^2, it is concluded that the 10^8 atoms/cm^2 level analysis is possible.

3.4 Metallic impurity effects on defect generation

The effects of transition metals on defect generation was made clear by the experiment as the following. Partially intentional contamination was treated by coating equal quantity of Fe, Ni and Cu on separate position of one wafer. This technique is invented to exclude the influence of wafer difference and oxidation condition. In this way, sample wafers with four contamination levels (10^{10}-10^{13} atoms/cm^2) were prepared. After the TREX analysis, they were oxidized at elevated temperature, and the OSF (Oxidation-induced Stacking Fault) density was measured at each contaminated position. The OSF density has a clear dependence on the metal concentration

analyzed by the TREX (Fig.6).

It was found that the density of OSF induced by Fe is hundreds times higher than those induced by Ni and Cu, that is, Fe effects strongly on OSF generation. Figure 6 also shows that the OSF density on ion implanted wafer followed by intentional contamination is about several hundreds times higher than the wafer without damage, that is, the damage induced by ion implantation enhances the generation of OSF. It is evident that there exists collaboration effect between the contamination and damage on defect generation.

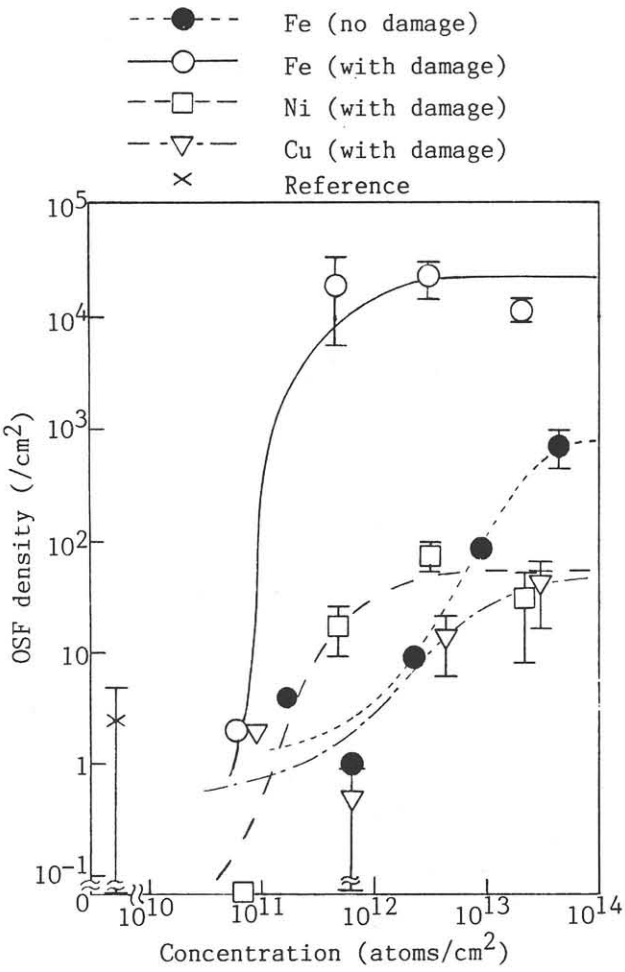

Fig.6 OSF density vs. metal concentration. Reference shows the OSF density on wafers without contamination. Solid circles are the OSF density on wafers without damage. Open circles, squares and triangles show the OSF density on damaged wafers.

4.CONCLUSION

A nondestructive evaluation method for trace metals on semiconductor wafers by the TREX has been established. The TREX enables distribution analysis and trace analysis as low as 10^{10} atoms/cm^2

The advantage of the TREX is proved by the application to the analysis of residual and adsorbed impurities on wafers, because the TREX is free from sample pre-treatment and needless to consider collection efficiency. The metal effects on crystal defect generation were made clear by using the same wafer with the combination of the TREX and a partially intentional contamination technique. These application prove that the in-process monitoring of an identical wafer has been very significant in device fabrication process and that can be established by the nondestructive analysis such as TREX.

Further improvement of the LLD as low as 10^8 atoms/cm^2 is confirmed by the combination of the TREX and impurity condensation with a chemical drop.

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