Determination of Oxygen in Semiconductor Silicon by Gas Fusion Analysis GFA - Historical and Future Trends -

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Interstitial oxygen is a relevant component of defect engineering. During Czochralski (CZ) crystal pulling, the silicon melt corrodes the quartz wall of the crucible to silicon monoxide. In that volatile form, oxygen will be partly included in the silicon ingot, partly removed by an inert gas flow from the crystal puller.
The oxygen [O_i] occupies interstitial position, increases the mechanical stability of the silicon wafer and, by designed heat treatment i.e. precipitation, facilitates gettering of metallic contamination from the active device zone of the wafer. Due to gettering defect density e.g. stacking faults (SF) can be reduced. The characteristic [O_i] concentration range is 10^{16} to 10^{17} [atoms/cm³] for CZ and <5 10^{15} [atoms/cm³] for float zone (FZ) silicon ingots. The analyst must be able to determine [O_i] in practical range of 10^{17} down to 10^{15} [atoms/cm³].

In the last two decades gas fusion analysis (GFA) became the routine method of [O_i] analysis of heavily doped silicon materials in which the free carrier absorption interferes with Si-O absorption.
GFA is a carrier gas heat extraction method for oxygen in alloys or in pure metallic substances. A silicon chip (500 mg) is melted in a small pure graphite double-crucible under helium carrier gas flow at 1600°C. The graphite reduces the silicon oxide in the melt and converts it to CO and CO_2. A catalyst oxidizes the CO to CO_2 and the oxygen concentration in the carrier gas can be determined by infrared absorption in a gas cell.
This method provides an inexpensive technique to determine [O_i] independent of dopant concentration. Independent complementary methods such as FTIR and SIMS are regularly used for correlation and, resp., certification of the GFA method.

Since 1986 a few millions of samples were tested by GFA in the quality assurance (QA) of the Wacker Siltronic AG. Crucial improvements occurred in sample treatment and handling, measurement procedure, calibration procedure with certified amounts of reference gas (100% CO_2) by mass flow controller (MFC), programmed temperature ramping to separate surface and bulk oxygen, integrated statistical treatment of data, etc. allowing the determination of 1 to 3 [µg] $O_{absolute}$ with an RSD of 1 %; in the range of 3 to 10 [µg] < 0.5% RSD.

For the realization of scientific oxygen analysis in referenced range a new instrumental concept (LECO TC 600 Series) has been developed by LECO. For semiconductor silicon, due to the modular construction, the instrument TC 600 can co-analyze nitrogen and hydrogen using different detection methods. The standard equipment can also analyze oxygen in steel, metallic oxides etc. down to < 10 [µg/g] or even nitrogen in proteins.
Programmed ramping provides a feature of separating surface native oxide and bulk silicon oxide. However, due to variation in the native oxide structure, the overall integral oxygen amount may still vary. Robust reproducibility needs more experimental efforts.

In order to meet demands for automation an automated crucible and sample service port (autosampler), cell cleaning (autocleaner) have been developed. Data management, including the gas calibration, allows the integration of the instrument into standardized QA network.

Keywords
Gas Fusion Analysis (GFA), Carrier Gas Heat Extraction, Gas Calibration, Mass Flow Controler, Silicon, Czochralski (CZ), Float Zone (FZ), Oxygen, O_i, FTIR, SIMS;