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Estimation of Carbon Substitutional Concentration in Czochralski-grown Silicon by means of Deep-Level Transient Spectroscopy and Infrared Spectroscopy Measurements

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Abstract

IR spectroscopy is so far the most commonly employed technique for measuring the carbon concentration in Si material. The current standards are based on the intensity of the 607 cm^{-1} line of the carbon substitutional (C_s). However, this carbon line is superimposed by a very intensive lattice vibration limiting the technique to C_s concentrations larger than 2 x 10^{16} cm^{-3}. In this paper a combination of optical (IR) and electrical (DLTS) measurements is suggested for measuring carbon content in Si below the present detection limit of ≈ 10^{16} cm^{-3}.

1. Role of carbon in control of process - induced defects in silicon

An important aim of "Defect Engineering" at manufacturing integrated circuits is to reduce the growing and process-induced fluctuations of material properties for stabilization of device technology and essential parameters [1]. This presupposes a deep physical insight into processes which are going on in semiconductor silicon during crystal growth and device processing and their influence of device parameters.
Cz-Si-crystals up to 300 mm (12") in diameter and 150 mm (6") for FZ-Si are grown at present. Cz-Si is the main basic material for microelectronics, 6" and 8"-Cz-Si-wafers being primarily used in fabrication lines. The demands made on the initial quality of the wafers have strongly increased in the past few years. This relates to the structural, mechanical, chemical as well as the geometrical parameters. For todays in silicon-device-technology two groups of extrinsic point defects are essential:

* oxygen and carbon exist in monocrystalline silicon and acting as nuclei for the formation of structural defects
* fast diffusing process-induced metals are decorating structural defects.

The structure defects formation makes silicon wafers to be a variable which is difficult to control in a device process. That complicates technology control under processing condition as well as process-simulation in stage of technology development. Therefore a reproducible and controlable material quality within the wafers, wafer to wafer, and crystal to crystal is demand [2]. In response to these requirements a multizoned wafer concept has been developed (Fig. 1). The defect formation is strongly related to the oxygen and carbon content of silicon. Oxygen is the major impurity and carbon a subsidiary impurity influencing silicon's mechanical strength as well as the nucleation and growth of oxygen precipitates.

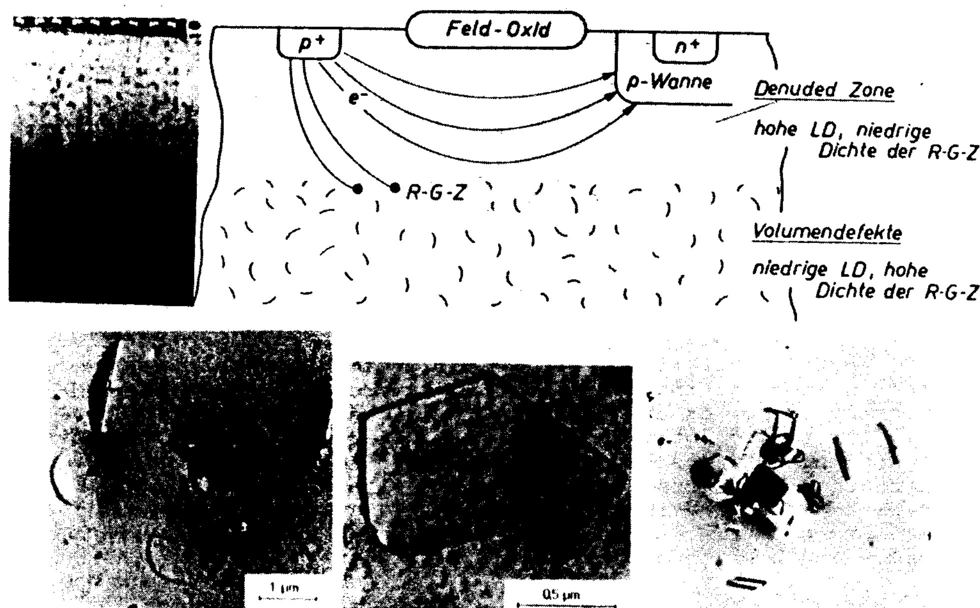

Fig. 1: Multi-zone wafer structure in silicon wafer

A variation of oxygen and carbon within a crystal can cause quality change from wafer to wafer and also within one and the same wafer.
In Cz-Si oxygen is present in concentrations ranging between $5 \cdot 10^{17}$ and 10^{18} cm^{-3} [3]. The carbon content is usually $\leq 2 \cdot 10^{16}$ cm^{-3} (for carbon-rich silicon $5 \cdot 10^{16} \ldots 5 \cdot 10^{17}$ cm^{-3}), but for ULSI technologies even silicon wafers with carbon concentration down to $5(2) \cdot 10^{15}$ cm^{-3} are required. In comparison to oxygen, carbon is much more difficult to detect by analytical techniques. Since its presence affects the yield and properties of Si devices [4,5] it will be very useful to know the exact C content of the various wafers.

The infrared spectroscopy is the most commonly employed technique for measuring the carbon concentration in silicon material. These measurements are based on the 607 cm^{-1} absorption line of the substituional carbon in silicon. The detection limit of this method is about few 10^{15} cm^{-3} for thick samples [4]. To measure carbon concentrations below this limit we suggest a combination of infrared (IR) and Deep Level Transient Spectroscopy (DLTS) measurements using the properties of irradiation-induced carbon related defects and heat treatment-induced oxygen-carbon clusters.

2. Irradiation induced defects

After irradiation the carbon intersitial C_i is produced through the reactions: S + irradiation --> Si_i, $Si_i + C_s$ --> C_i + Si. C_i gives an absorption [6] at 922 and 932 cm^{-1}. At around R. T., C_i becomes mobile. One trap for the migrating C_i is the C_s.

The resulting C_i-C_s pair gives a luminescence line at 969 meV (G-Line) and the G11-EPR signal. An electrical level at E_v + 0.34 eV [7] was initially attributed to the C_i-C_s pair. Recent papers [8] correlate two levels at E_v + 0.09 eV and E_v+0.05 eV with the C_i-C_s pair and leave the assignment of the E_v + 0.34 eV level in question. The defect alternate between two configurations exhibiting charge dependent amplitudes in the DLTS spectra. Up to now only E_v + 0.09 eV level has been detected by DLTS. In Cz-Si, O_i is also a trap of the C_i atom. The resulting C_i - O_i pair is IR active (865.2 cm^{-1} and 1115.5 cm^{-1}), gives the G15-EPR spectrum and the E_v + 0.35 eV level [9] detected by DLTS.

C_s causes at room temperature a local vibration at 607 cm^{-1} from which its concentration could be calculated. However this carbon band is superimposed by a very intensive lattice vibration (intrinsic two-phonons band). The detection limit of the procedure is about few 10^{15} cm^{-3} and as previously mentioned, the exact knowledge of the Carbon concentration below this detection limit will be of large practical value. A few attempts have been made in the past in this direction. In one investigation [10] an experimental calibration curve was given correlating C_s content with the C(3) and 790 meV lines of the C_i-O_i center which occur in spectral regions where there is only weak underlying structure. In another investigation [11] DLTS measurements have been used to correlate the C_s content with the E_v + 0.34 eV concentration of the C_i-C_s pair. However the above assignment is now seriously doubted [8]. Photoluminescence measurements concerned the 970 meV, G-line of the C_i-C_s pair in conjunction with IR mesurements of the C_s content were also employed [12].
In DLTS measurements one could measure deep levels concentrations as low as 10^{11} cm^{-3}. In this context, the scope of the present work is to suggest a combination of IR and DLTS measurements in order to create a calibration curve correlating the C_s content with the concentration of the E_v + 0.09 eV level of the C_i-C_s pair in p-type Si. In a Si material with C_s content below the IR detection limit one will measure the C_i-C_s concentration by DLTS and then the carbon concentration will be estimated from the extrapolated part of the calibration curve. The general outlines of this proposal appear as follows:

3. On the relation between C_s and C_i-C_s

For the experimental investigations of this relation carbon-lean Cz-Si samples should be used. By exploiting the effect of oxygen-carbon clustering [13] at temperatures of heat treatment of about 600 °C we can obtain a set of samples with different concentrations of substitutional carbon [C_s]. The decrease of [C_s] due to heat treatment allows some extrapolation below the detection limit of the IR-measurements of about few 10^{15} cm^{-3}.
The samples will be irradiated at room temperature with electrons of an engergy E = 1.5 - 3.5 MeV and various doses in the range 10^{15} - 10^{16} e/cm^2. After the electron irradiation the samples should be measured by IR to estimate possible change in [C_s].

The DLTS measurements will be carried out on the same samples as the IR measurements. The DLTS temperature scans below the temperature of liquid N_2 will be performed in search for the irradiation induced H (0.09) and H(0.05) levels which are ascribed to the C_i-C_s pairs. This assignment will be verified by the exhibition of charge dependent amplitudes [8] of the peaks in

the DLTS spectra. In this way the concentration of the C_s should be compared with the C_i-C_s concentrations for Cz-Si samples with different oxygen concentrations.

This calibration allows to measure $[C_s]$ by means of DLTS. The practical limits of the proposed procedure will be probably affected by the oxygen-carbon clustering for higher oxygen and carbon content. On the other hand, the linearity of the calibration curve will also be affected for carbon content below 10^{16} cm^{-3} where boron emerges besides the C_s as an other potential candidate for capturing the C_i.

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