Measurement of carbon concentration in silicon crystal
(XXI) Concentration reduction and improvement of infrared absorption measurement for carbon engineering

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シリコン結晶中の低濃度炭素の測定（ＸＸＩ）炭素濃度の低減と測定法の進歩：Carbon engineering

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1 In 1980's, LSI period: Carbon reduction and standard revision for "detection limit of 5x10^{14}/cm^3"

(1) Till the beginning of the LSI period in about 1975: In Tr & IC (and diode) period, carbon was considered to be an origin of the swirl defects both in FZ and CZ Si and hence its reduction was important. Carbon was reduced by (a) suppressing the formation of CO in the furnace and by (b) promoting the removal by the gas flow.

(2) In the beginning of the LSI period: The carbon concentration was still high, around 10^{16}/cm^3, but did not affect the defect density as far as it was below 10^{16}/cm^3. "Useful range" of the infrared (IR) measurement ASTM standard was 5x10^{15}/cm^3 at RT [1]. Oxygen reduction was mainly examined to remove swirl defects [2], by the same way as above. It was most important to keep the temperature of the carbon heater and silicon (poly and melt), especially during melting, as low as possible. Later, it became important to control the oxygen concentration. Therefore the dissolution of oxygen to the melt from the quartz crucible was the main concern [3]. The control of the melt flow by the magnetic field became the main topic [4]. Kolbesen examined the low temperature IR measurement [5]

(3) Around 1980: Low pressure CZ furnace was introduced for the larger diameter crystal growth [3]. Large melt and long growth time resulted in the dislocation introduction due to the SiO_2 particles dropped on the melt surface. Reduction of the formation and elimination by the gas flow were necessary, again the same for carbon. In 1979, Zulehner introduced the heat shield, cover over the melt surface, to prevent the SiO_2 particle drop [6]. It, however, made the gas flow nearer to the melt surface. Therefore, the carbon introduction to the melt and elimination by gas flow were studied in detail [7]. This problem was solved depending on the growers. As a result, dislocation suppression provided the carbon reduction in 1980's. Thus, the concentration in commercial wafer was either below or above 1x10^{15}/cm^3, the latter being the majority, till about 2015. LSI people did not mind the carbon concentration seriously.

As for the measurement, FTIR became popular and low temperature measurement drew attention. The ASTM standard was revised for such trends including the JEIDA activity in 1980's using a reference of (a) **4x10^{15}/cm^3** [8]. The "detection limit of 5x10^{14}/cm^3" was introduced [9, 10]. It is defined in the standard as: Limit of detection (LOD): lowest concentration that can be detected by an instrument, with explanation: LOD is typically defined as three times the standard deviation of the mean noise level [11]. In the standard it is described, in short, that the detection limit is determined by the concentration in the reference sample, at (b) **2x10^{15}/cm^3** (equal to the concentration of the reference of JEIDA standard sample sets in 1990's), agreeing with the review by Kolbesen [12]. Until about 2015, many people could not use the reference below 1x10^{15}/cm^3 (equal to the sensitivity of ordinary CPAA). It was practically difficult to measure the concentration below 1x10^{15}/cm^3 as written in the standard "measurement near the detection limit is comparative only" (the most fundamental reference problem). In the system on silicon period from 1995, carbon was not a problem.

2 From 2000's, Power device period: Carbon control and reduction and IR detection limit to 1x10^{13}/cm^3

(4) Around 2005 hybrid car opened the power device period [13]: Radiation induced C_iO_i is used for lifetime control of some devices (C_iO_i engineering), whereas carbon affects the performance of another device [14]. Control and reduction (base for carbon engineering) became important. We performed the high sensitivity IR analysis of C_iO_i down to 10^{12}/cm^3 with power device researchers [15].

As for the measurement, sensitivity in the comparative measurement was improved to 10^{14}/cm^3 in 2005, but the "assumed content" of our reference was (c) **5x10^{14}/cm^3** [16]. Sensitivity improvement is continued utilizing the techniques for the nitrogen concentration measurement standard (unwanted peak deletion) [17] and for the infrared defect dynamics. Fabrication of synthetic reference sample by electron irradiation (we used about (d) **1x10^{14}/cm^3** known content and the top data is about (e) **1x10^{13}/cm^3** [19]) made the detection limit limitless and made the measurement of net content possible [18, 19]. SIMS [20] improved the IR reliability. Evaluation of machine performance was established [21]. Finally, the measurement of polycrystalline silicon including it at low temperature [22, 23] was improved under the collaboration with the foregoing researchers [19]. In many leading companies measurements are daily performed now for both single- and poly-crystal down to 1x10^{14}/cm^3 [19]. The above novel techniques were added to the existing standard for convenience [24] and is examined by the collaboration with crystal suppliers, IR experts, IR machine suppliers and SEMI in the world. In summary it is shown that the concentration reduction and sensitivity improvement always work together.

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