Measurement of carbon concentration in silicon crystal/ 2-nd generation
(28) Solution of middle and inner phonon band problems in infrared absorption (1)

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シリコン結晶中の低濃度炭素の測定/第二世代(28)赤外吸収の middle, inner phonon band 対策 (1)

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Low temperature IR, base of science and society

In 2019, the isotope-enriched silicon sphere replaced the kilogram prototype [1]. About 2x 1014/cm3 carbon is included in it [2], changing lattice parameter, affects the accuracy of kilogram unit. **Measurement of carbon concentration in Si became the base of science and society** which is performed by **low T infrared absorption (IR) according to the ASTM Standard** [3]. **Low temperature IR measurement** is widely used in leading Si suppliers since '70s [4-8].

1-st Generation IR for LSI period

In 1975 LSI (DRAM) research projects started. We began IR study and established two basic procedures: (1) 560-640 cm-1 baseline and (2) 0.8x1017/cm2 calibration factor [9] Unknown carbon concentration in the reference and the calibration factor were determined statistically assuming the result of CPAA was correct. All results of the round-robin measurement were used without checking the performance of the individual instrument. Our proposal was included in the ASTM Standard revision in 1990 [10] in which the instrumental detection limit was assumed to be 5x1014/cm3. It turned into the existing SEMI Standard. It was confirmed that carbon does not affect the defects in Si below 1016/cm3 [11]. Carbon did not take attention in the LSI period.

2-nd generation IR for power device period Around 2005, power device in the hybrid car took attention. It utilizes the radiation-induced CO pair [12]. We have developed the **2-nd generation IR for the "power device period**" since 2005 when we measured 1014/cm3 at RT [13]. There are three key techniques, (1) **preparation of carbon-free reference sample** established in 2008 [14], (2) **way to estimate the instrumental detection limit** shown in 2021 [15], and (3) **solution of the interfering fractional phonon band problem** established in 2016 [16]. The basic part was transferred to world's leading Si suppliers through the round robin measurement using samples with C down to 1014/cm3 [17].

There are three kinds of phonon bands (1) outer at 575 and 625 cm-1, (2) middle at 612 cm-1 and (3) inner phonon bands at 600 and 608 cm-1, located at the inflection points of the phonon absorption band [16]. The outer phonon bands are distinct at concentration above 1015/cm3, but are well separated from the carbon band. Drawing the baseline within the outer phonon bands between 590 and 618 cm-1 solves the problem [16]. We call it the middle baseline and call the conventional 560-640cm-1 as the long baseline. Middle phonon band becomes comparable to the carbon band of around 5x1014/cm3 concentration. Both bands overlap at the intermediate region. Fortunately, the middle phonon band is nearly 0 at the carbon peak, and does not affect the carbon peak height. The middle baseline is the solution also. Measurement of 2-3x1014/cm3 was established by this procedure.

Inner phonon bands are comparable and too close to the carbon band at C concentration around 1014/cm3 at RT. We have developed the solution as will be described in detail in the next time. Short baseline between 600 and 610 cm-1 works well at RT.

(3) **Low temperature IR measurement** is widely used in leading Si suppliers since '70s. We found its new advantage, separation of the inner phonon bands from the carbon band due to sharpening at liq. N temperature. Measurement of 1013/cm3 was demonstrated [18]. Calibration for liq. N temp is necessary. (4) **Measurement of poly-Si** down to 1014/cm3 was also established [8]. We thank Hemlock Semiconductor Operations LLC (USA) for collaboration in sample preparation and low T measurement and Prof. Kolbesen for discussion.

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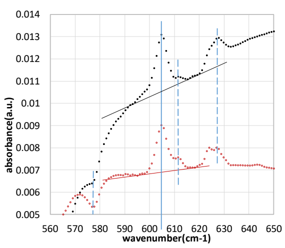

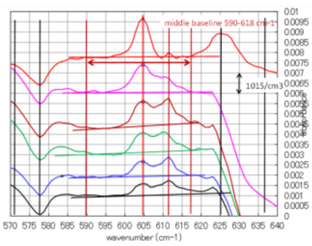

Fig. 1Outer phonon bands at 575 and 625 cm-1 and middle baseline. Fig. 2 Middle phonon band at 612 cm-1 and middle baseline.