一般セッション(口頭講演) | 15 結晶工学：15.7 結晶評価，不純物・結晶欠陥

2025年3月14日(金) 13:30 ~ 14:15 K306 (講義棟)

[14p-K306-1~3] 15.7 結晶評価，不純物・結晶欠陥

平野 愛弓(東北大)

13:30 ~ 13:45

[14p-K306-1]

シリコン結晶基板の品質と点欠陥 第二世代 (13) 点欠陥に対する内部応力効果

〇井上 直久[1]、川又 修一[1]、奥田 修一[1] (1.大阪公大放射線研究センター)

13:45 ~ 14:00

[14p-K306-2]

シリコン結晶の高感度赤外吸収と赤外欠陥動力学/第二世代 (26)シャロ-サーマルドナーの赤外吸収

〇井上 直久[1]、川又 修一[1]、奥田 修一[1] (1.大阪公大 放射線研究センター)

14:00 ~ 14:15

[14p-K306-3]

シリコン結晶中の低濃度炭素の測定/第二世代(30)赤外吸収のinner phonon band対策、液体窒素温度測定

〇井上 直久[1]、奥田 修一[1]、川又 修一[1] (1.大阪公大 放射線研究センター)

Quality of silicon substrate and point defects: 2nd generation
(13) Effect of internal stress on point defects

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シリコン結晶基板の品質と点欠陥 第二世代 (13) 点欠陥に対する内部応力効果

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In 1960, Bond and Kaiser revealed the lattice expands with O concentration and suggested that O occupies an interstitial site [1]. In 1968, Baker et al. revealed the lattice contraction due to C substitutional [2]. In 1971, we clarified the 10^{-6} lattice nonuniformity in synthetic quartz due to Na impurity [3].

In 1983, Abe et al. pointed out the effect of stress field due to large temperature gradient at the solid-liquid interface in growing Si crystal on intrinsic point defect [4]. In 1986, Chikawa, Abe and Harada found that the interstitial type or vacancy type microdefect is observed in highly doped Si of either smaller or larger atom [5].

In 1999, we theoretically and quantitatively analyzed these two internal stress effects on the type of microdefects [6, 7, 8]. We extended the stress field model around dopant by Rytova [9].

Equilibrium V (vacancy) concentration under compressive internal stress is shown by the following equation.

$$Nv = Nvo \exp\ (16Qr_o^3 N_d / kT)\quad Q = K|V_d - V_{Si}| \quad (1)$$

Here, r_o is range of stress around the impurity, Q is potential well height, K is fitting parameter, N_d is dopant and V is atomic volume. By fitting to the experimental result, it was shown that only 0.1% increase of V or I concentration produces V or I type defect as shown in Fig. 1 [6, 7]. DeKock proposed the electronic effect [10]. Sueoka followed, but later adopted stress effect [11]

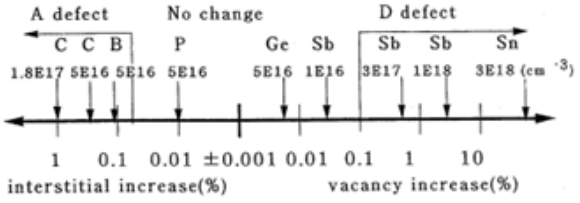
Axial internal stress σ_z by the temperature gradient at the growing interface changes the (equilibrium) V concentration as in the following equations [6, 8].

$$\sigma_z = -\alpha E/(1-\nu)\{\partial^2 T/\partial z^2 - T\} \quad (2)$$

$$C^{eq}/C_0^{eq} = \exp(\sigma \Delta V_R/kT). \quad (3)$$

Here, α is expansion coefficient, E is Young's modulus, ν is Poisson ratio and ΔV_R is the relaxation volume, about 1/3 of Si atomic volume. We used E = 8.45MPa at the melting point derived from the existing data [12] and obtained the increase of 0.006% as shown in Fig. 2 [6, 8]. Larger effect in larger diameter crystal was predicted [6, 8]. In 2000, measurement of E upto 1000 ºC was reported not decease as much as expected [13], and in 2013 E upto 1400 ºC was reported, 100 GPa [14], 4 orders of magnitude larger than the previous evaluation. By using this 0.1% increase of V is supplied when σ is 17.3 MPa. In 2014, Shift from Voronkov's criterion [15] in large diameter crystal was reported and attributed to the internal stress field [16]. The calculated stress was around 10 MPa. It confirmed our prediction. In 2014, Vanhellemont followed our analysis, but treated by the external stress and got the opposite result [17]. 10% larger ΔV_R gives 10% smaller σ.

[1] Bond and Kaiser, J. Phys. Chem. Sol. 16, 44 (1960). [2] Baker et al. J. Appl. Phys. 39, 4365 (1968). [3] Takano and Inoue, J. Cryst. Soc. J. 13, 344 (1971). [4] Abe et al. Physica B+C, 116, 139 (1983). [5] Chikawa et al. Electrochem. Soc. Proc. PV 86-4, 61 (1986). [6] Inoue, Tanahashi, Mori, J. Japan. Assoc. Crystal Growth, 26, 242 (1999). [7] Kikuchi et al. Electrochem. Soc. Proc. PV 99-1, 491 (1999). [8] Tanahashi et al. J. Crystal Growth, 210, 45 (2000). [9] Rytova et al. Sov. Phys. Semicond. 20, 869 (1986). [10] de Kock J. Cryst. Growth 49 (1980) 718. [11] Sueoka, J. Surf. Sci. Soc. Japan, 37, 116 (2016). [12] Wijaranakula, J. Electrochem. Soc. 140, 3306 (1993). [13] Ono et al. Japan. J. Appl. Phys. 39(2R) 368 (2000). [14] Swamakar et al. phys. stat. sol. c, 11, 150 (2013). [15] Voronkov, J. Crystal Growth, 59, 625 (1982). [16] Nakamura et al. ECS Sol. State Lett. 3(3), N5 (2014). [17] Vanhellemont, J. Appl. Phys. 110, 063519 (2011).



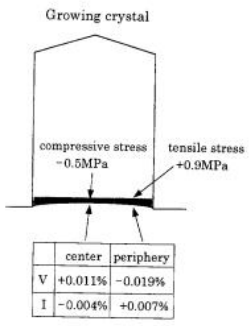


Fig. 4 Stress distribution and point defect concentration during growth.

High sensitivity infrared absorption spectroscopy and infrared defect dynamics of silicon crystal/ 2-nd generation (26) LVM IR absorption of shallow thermal donor

シリコン結晶の高感度赤外吸収と赤外欠陥動力学/第二世代 (26) シャロ−サーマルドナーの赤外吸収

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In 1968, shallow donors were found in annealed N-doped FZ Si [1]. In 1986, 5 electron transition absorptions were observed in CZ-Si and their thermal behavior was reported [2, 3]. In 1996, two types of models were proposed by a theorist group, (NO) ring (N_i-Si-O_i-Si rectangle, [4]) and (ONO) double ring [5]. In 2001, 1 N inclusion was supported and STD was suggested to be dominant in low N Si [6], although (NN) ring is dominant in high N Si [7]. Sum of two STD absorption at 240 and 250 cm^{-1} was proposed to measure N concentration in low N Si [8].

We examined LVM IR absorption of STD. In 2003, quasi equilibrium among (NN), (NN)O and O(NN)O in annealing was reported [9]. We examined the same annealed samples and found candidates at 714, 736, 841, 855, 862, 941, 945, 973, 1002, 1008, 1065 cm^{-1} in 2004 as shown in Fig. [10]. In 2005, we reported 3 of them at 855, 973 and 1002 cm^{-1} and assigned 973 and 1002 cm^{-1} as O(NO)O from the O(NN)O like thermal behavior [11, 12, 13]. We asked the theorists to calculate LVM. In 2007, they reported the results on (NO), (NO)O and (ONO), and assigned the observed 973 and 1002 cm^{-1} as (NO)O and 855 cm^{-1} as (ONO) [14].

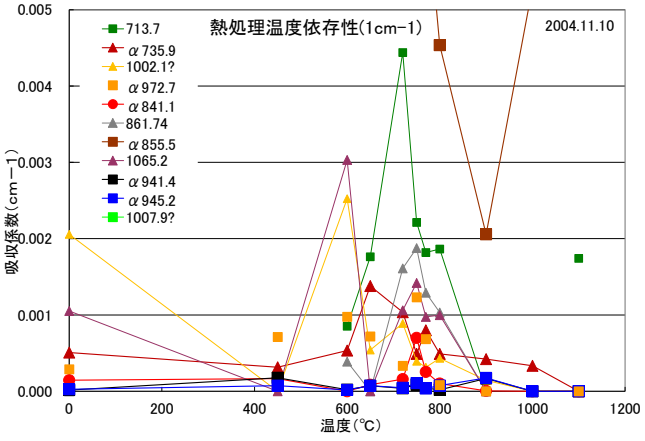
The problem arose, 973 and 1002 cm^{-1} absorption behavior suggests 2 O accompanying with (NO) and 855 cm^{-1} accompanies at least 1 O. (ONO) must be largest at 800 ºC, conflicting with the observed thermal behavior.

We composed 5 models for STD; (NO), (NO)O, O(NO), O(NO)O and (ONO). We took care (1) N-O-3 at 240 cm^{-1} and N-O-4, 5 at 242 and 250 cm^{-1} remain after annealing at 800 ºC, suggesting no O accompanies. (2) Thermal behavior of N-O-3 deflects around 600 ºC [2, 3]. We interpreted it due that there are low-T type and high-T type. For (2), we examined absorption around 855 cm^{-1}. Previously observed 840 and 862 cm^{-1} absorption (Fig.) shows peak at 800 ºC. Therefore, we concluded that 855 and 1065cm^{-1} absorption comes from O(NO) and 840 and 863 cm^{-1} from (ONO).

For (1), We examined high-T absorption at 714 cm^{-1}. In 2018, we reported it from irradiated and annealed O-rich NFZ samples and named it 800 ºC group [15]. It must be (NO) originated. (NO)O absorption is left. It may locate at 10-20 cm^{-1} higher frequency. 739cm^{-1} absorption is the candidate. Like other absorption it overlaps the strong phonon bands, making analysis difficult. Table summarizes the identification of STD LVM IR absorption bands and correspondence with electron transition. There are low-F H_2O type and high-F BF_3 type LVM for all STDs. More absorption will be assigned.

[1] Zorin, Sov. Phys. Semicond. 2, 111 (1968). [2] Suezawa, JJAP, 25(10A), L859 (1986), [3] Suezawa, JJAP, 27(1R), 62 (1988). [4] Ewels, Phys. Rev. Lett. 77, 865 (1996). [5] Gali, J. Phys. Condens. Matt. 9, 7711 (1996). [6] Voronkov, J. Appl. Phys. 89, 4289 (2001). [7] Porrini, ECS Proc. 2003-03, 75 (2003). [8] Jones, Phys. Rev. Lett. 72, 1882 (1994). [9] Tanahashi, JJAP, 42 Pt. 2, L223 (2003). [10] Inoue, unpublished (2004). [11] Inoue, Solid State Phenomena, 108-109 (2005) 609. [12] Inoue, Physica B, 376, 101 (2006). [13] Inoue, Materials Science and Engineering, B134, 202 (2006). [14] Fujita, Physica B, 401-402,159 (2007).-[15] Inoue, JAP, 123, 185701 (2018).

(NO)Om	Comp.	LVM	STD	(NN)Om	Tmax
NO	NO	714[1,2]	N-O-4,5 242, 250	(NN) 766,963	800
(NO)O	NO2	739[1]	-	(NN)O 801,996,1027	600
O(NO)	NO2	855, 1064[1]	N-O-3 240	ibid	600
(ONO)	NO2	840[1], 862[1]	N-O-3 240	ibid	800
O(NO)O	NO3	973, 1002	N-O-1,2 234, 237	O(NN)O 810, 1018	600



Measurement of carbon concentration in silicon crystal/ 2-nd generation

(30) Solution of inner phonon band problem in infrared absorption (2) Liquid N-T measurement

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シリコン結晶中の低濃度炭素の測定/第二世代(30)赤外吸収の inner phonon band 対策、液体窒素温度測定

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IR absorption is practical as well as scientific measurement technique of carbon concentration in Si [1]. Low temperature measurement at liquid N T was dominant especially in early days [1, 2, 3] and adopted in the ASTM Standard [4], as summarized in Tab. Four representative papers were from single and poly-Si suppliers [2, 3, 5, 6] showing the easiness of measurement at liq. N T. Moreover in 2011, measurement on the Avogadro crystal for $2x10^{14}/cm^3$ was reported [7]. It established as the base of science: Carbon concentration determines the accuracy of Avogadro number and International System of Units [8]. It was said that low T measurement is advantageous for phonon overlapping problem [7].

We have established RT measurement in 1987 [9] and the results consisted ASTM Standard prepared for FTIR in 1990 [4]. In 2005 we demonstrated measurement of $10^{14}/cm^3$ at RT [10]. In 2016 we identified the middle and inner phonon band problem at RT [11]. In 2018, we reported the LT measurement of $10^{13}/cm^3$ for single crystal [12]. 5 4mm thick samples with [C] lower than $1x10^{14}/cm^3$ were measured, and differential absorption spectra of all pairs are shown in Fig. Though interference fringes are observed, the inner phonon bands do not interfere for most spectra. C concentration was obtained to be 10, 9, 6, 4, $1x10^{13}/cm^3$, respectively. Instrumental detection limit (IDL, 3x standard deviation of measured difference from the expected value, [4, 13]) was about $1x10^{13}/cm^3$ and spectral detection limit [13] was $2x10^{13}/cm^3$, for this preliminary unoptimized measurement. IR enabled $10^{14}/cm^3$ measurement of poly-Si both at RT and LT, more sensitive at LT. Ratio between the absorption at RT and LT [14] must be redetermined using FTIR.

[1] Newman, J. Phys. Chem. Sol. 26, 373 (1965). [2] Baker (Dow Corning. (later Hemlock)), J. Appl. Phys. 39, 4365 (1968). [3] Endo (Komatsu), Anal. Chem. 44, 2258, (1972). [4] ASTM F-1391, SEMI MF-1391(1990). [5] Hwang (Hemlock), J. Electrochem. Soc., 138, 576, (1991) [6] Porrini (MEMC, Wacker), Solid State Phenomena, 108-109, 591 (2005). [7] Zakel, Metrologia, 48, S14 (2011). [8] International System of Units 9-th ed (2019). [9] Inoue, ASTM STP960, 365 (1987). [10] Inoue, Solid State Phenomena, 108-109, 632 (2005). [11] Inoue, Phys. Stat. Sol. C, 13, 842 (2016). [12] Inoue, ECS Trans. 86-10, 105 (2018). [13] Inoue, JSAP 2021A, 10p-N203-9. [14] Kolbesen, Solid State Electronics, 25, 759 (1982).

	RT	Low T*	poly
1965 Newman		8x1016	
1968 Baker#		1.3x10[16]	
1972 Endo	1x1017	1x1017	
1987 Inoue	2.8x1015		
FTIR			
1990 ASTM	5x1015	5x1014	
1991 Hwang#			1.5x1015*
2005 Porrini#		1x1015	1x1015*
2005 Inoue	1x1014		
2011 Zakel		2x1014	
2017 Inoue		1x1013	1x1014