

Spectroscopic parameters of LVM absorption bands of carbon and oxygen impurities in isotopic enriched silicon ^{28}Si , ^{29}Si and ^{30}Si

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The IR spectra of all three Si isotopes in the form of bulk single crystals (^{28}Si with enrichment more as 99.9%, ^{29}Si and ^{30}Si with enrichment more than 90%) has been studied at $T = 300$, 17 and 5 K in spectral range 550–1200 cm^{-1} . IR active local vibrational modes (LVM) of the $\text{Si-}^{12}\text{C}$ centered at 605 cm^{-1} and of $\text{Si-}^{16}\text{O-Si}$ quasi-molecules in region of 1136 cm^{-1} for all Si isotopes in comparison with Si of natural isotopic composition as well as its isotopic shift at 300 and 17 K have been determined. The dependence of shape of antisymmetric stretching vibration band of $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$ in spectrum of ^{28}Si on spectral resolution has been studied. The perspectives of generalization of IR spectroscopy method for determination of carbon and oxygen impurities in Si of natural isotopic composition to mono-isotopic Si have been discussed.

1. Introduction

Carbon and oxygen impurities are permanently present in silicon single crystals manufactured both by Czochralski (Cz) (the manufacturing process itself is the main source of impurities), and float-zone (FZ) method as well as by deposition from the vapor phase. The atoms of oxygen are located at interstitial positions of silicon crystal lattice at the concentration lower than that of solubility ($2 \cdot 10^{18} \text{ cm}^{-3}$ at the melting temperature) and the atoms of the dissolved carbon (solubility at the melting temperature is $3.5 \cdot 10^{17} \text{ cm}^{-3}$) are located at the lattice sites. Despite the fact that both impurities are not electrically active, the structure of the impurity in the lattice and concentration are of importance both to provide a controllable growth of silicon crystals and to apply Si in manufacture of semiconductor structures. It is known, as an example, that heat treatment of Cz-Si leads to formation of oxygen-containing thermal donors — electrically active centers affecting the main electrical parameters of this material [1] and playing a role of initial stage of formation of the second-phase inclusions (precipitates) [2]. The precipitates themselves become the source of a great amount of structural defects (e.g., of dislocations). The latter can also be „the intrinsic getters“ of the undesirable impurities in the process of manufacturing of semiconductor devices. It is also known [3] that carbon noticeably effects the precipitation processes of oxygen and its gettering functions. Besides, the impurities of oxygen and carbon present at the level of $3 \cdot 10^{15} \text{ cm}^{-3}$ even in high-purity silicon crystals, also lead to a certain distortion in

crystal site that can be essential at precision measurements of its parameters [4].

Locating at interstitial positions, the atoms of oxygen form a Si-O-Si quasi-molecule with the environment which originates an IR active local vibrational mode (LVM) with the maximum of the most intensive antisymmetric stretching band ν_3 at 1106 cm^{-1} at room temperature. The most intensive LVM absorption band of Si-C at 605 cm^{-1} at the same temperature is characteristic of carbon substitutionally incorporated into the silicon lattice. Both these bands overlap in different extent with the bands of intrinsic phonon absorption of Si. Special features of these and other less intensive absorption bands of oxygen and carbon at different temperatures and impurity concentrations are being in detail discussed in literature for many years (e.g., the reviews [5,6]). On the basis of these data the standard measurement procedures have been developed for IR spectroscopic determination of the impurities of oxygen and carbon [7,8].

The above-mentioned statements refer to the silicon samples of natural isotopic composition containing ^{28}Si 92.21%, ^{29}Si 4.70% and ^{30}Si 3.09%. It might be expected that in going to the samples of isotopically pure Si the noticeable changes in spectral parameters of absorption bands of oxygen and carbon will be observed due to changes in the lattice parameters and phonon spectrum. Earlier it was evidently demonstrated for the oxygen band at 862 cm^{-1} in isotopically enriched germanium (98% enrichment) [9]. Similar studies for mono-isotopic samples of Si are evidently of scientific and applied interest, first of all from the point of view of quantitative determination of

Table 1. Concentration (cm^{-3}) of oxygen and carbon impurities in reference silicon samples with natural isotopic composition according to IR inter-laboratory determination

Number of samples (thickness, mm)	Oxygen			Carbon		
	ICHPS (17 K)	PTB* (5.2 K)	Passport data	ICHPS (17 K)	PTB* (5.2 K)	Passport data
1 (2.21)	$\leq 3 \cdot 10^{14}$	$\leq 3 \cdot 10^{14}$	$(3.0 \pm 0.1) \cdot 10^{14}$	$\leq 3 \cdot 10^{15}$	$(1.8 \pm 0.9) \cdot 10^{15}$	$\leq 3 \cdot 10^{15}$
2 (4.02)	$(4.4 \pm 0.3) \cdot 10^{15}$	$(4.3 \pm 0.2) \cdot 10^{15}$	—	$\leq 3 \cdot 10^{15}$	$(2.0 \pm 0.3) \cdot 10^{15}$	—
3 (2.96)	$(2 \pm 0.1) \cdot 10^{15}$	$(1.9 \pm 0.2) \cdot 10^{15}$	$(1.8 \pm 0.1) \cdot 10^{15}$	$\leq 3 \cdot 10^{15}$	$(3.0 \pm 0.2) \cdot 10^{15}$	$3 \cdot 10^{15}$
4 (1.95)	$(3.1 \pm 0.1) \cdot 10^{15}$	—	$3.1 \cdot 10^{15}$	$(1.5 \pm 0.2) \cdot 10^{16}$	—	$(1.0 \pm 0.1) \cdot 10^{16}$
5 (0.37)	$(7.0 \pm 0.1) \cdot 10^{17}$	—	$(6.9 \pm 0.1) \cdot 10^{17}$	$< 1 \cdot 10^{16}$ (300 K)	—	—

*PTB — Physicalish-Technische Bundesanstalt

these important impurities. However, it was impossible to do it up to the latest time due to a lack of bulk samples of ^{28}Si , ^{29}Si and ^{30}Si with sufficient degree of purity, crystalline perfection and high enrichment. Experiments, including the investigation of IR spectra, with different silicon isotopes can now be realized due to the development of the technique [10,11] for production of high-purity mono-isotopic ^{28}Si as well as ^{29}Si and ^{30}Si [12].

The goal of the present work is to investigate IR absorption spectra of the carbon and oxygen impurities in single crystal samples of ^{28}Si , ^{29}Si and ^{30}Si of the record high isotopic enrichment (see below) at room temperature and at $T = 17$ and 5 K. One of the aims of this work was to find out the possibility to apply the above-mentioned standard techniques [7,8], developed for material with natural isotopic composition, for quantitative determination of the impurities of carbon and oxygen in mono-isotopic Si. It should be noted that then this study was in progress the paper of Kato et al. [13] has been published, there the high-resolution IR absorption study together with theoretical calculations of the LVM's of oxygen in isotopically enriched ^{28}Si (99.86%), 29 (97.10%) and ^{30}Si (98.74%) were reported.

2. Experimental

The bulk single crystal samples of mono-isotopic ^{28}Si , ^{29}Si and ^{30}Si were investigated. The starting polycrystals were obtained by the technique [10] at the Institute of Chemistry of High-Purity Substances (ICHPS) (Nizhny Novgorod) from silicon tetrafluoride enriched in Science-Technical Centre Electrochemical Plant (CENTROTEKH, St. Petersburg). The single crystals were grown at the Institute of Crystal Growth (Berlin) by combination of Cz-method and the crucibleless FZ-method (^{28}Si) or only by Cz-method (^{29}Si and ^{30}Si). According to the laser ionization mass spectrometry the enrichment of the studied ^{28}Si samples was on the average equal to 99.91%. The enrichment for ^{29}Si was 99.86%, ^{30}Si — 99.74%. The samples were of n -(^{29}Si , ^{30}Si) and p -(^{28}Si) type conductivity and contained (by the data of IR spectroscopy) electrically active impurities (B, P) at the level of $\sim 10^{14}$ – 10^{15} cm^{-3} .

The commercial samples of Si of natural isotopic composition with the impurity content and structural perfection, close to the samples of mono-isotopic Si (Table 1), were used as reference samples.

The samples investigated were in the form of plane-parallel discs with diameter of 8–12 mm and thickness of 0.37–2.2 mm. During preparation of the samples for IR measurements they were grinded and mechanically polished with diamond powder of $1 \mu\text{m}$ dispersion.

The absorption spectra were recorded by IFS-113v (ICHPS) and IFS-66 (PTB) IR spectrometers with spectral resolution of 1 cm^{-1} ($T = 300 \text{ K}$); 0.5 cm^{-1} (5 K); 0.5 , 0.3 and 0.1 cm^{-1} ($T = 17 \text{ K}$) in the spectral range 500 – 1400 cm^{-1} and Happ Genzel apodization function.

The sample were cooled down to the temperature of 16 K using RGD 210 (ICHPS) refrigerator-cryostat and down to 5 K using Optistat CF helium flow-through cryostat (PTB).

3. Results and discussion

3.1. IR absorption spectra of C and O in Si of natural isotopic composition ($^{\text{nat}}\text{Si}$)

Due to the fact that the measurement of spectra was carried out in two different groups on various equipment with goal to determine the reproducibility of results, an inter-laboratory experiment was carried out on investigation of impurity spectra of carbon and oxygen in five samples of single crystal silicon with natural isotopic composition. In four samples for oxygen and three samples for carbon the content of impurities was determined independently (Table 1). The necessity of these measurements was also due to the fact that the known calibration coefficients, used in standard analytical techniques for determination of the impurities of C and O in silicon [7,8], refer to room temperature. At the same time a sufficiently low level of the mentioned impurities in mono-isotopic samples necessitated the measurements at low (below 20 K) temperatures. The literature data on calibration coefficients at these conditions are rather contradictory, at least with respect to the impurity of oxygen [5,14].

Table 2. Spectral positions (ν_{\max} , cm^{-1}) of phonon modes in IR spectrum of silicon with natural isotopic composition ($^{\text{nat}}\text{Si}$) and of mono-isotopic Si at $T = 300\text{ K}$

Phonons	$\nu_{\max} (^{\text{nat}}\text{Si})$ [4]	$\nu_{\max} (^{\text{nat}}\text{Si})$	$\nu_{\max} (^{28}\text{Si})$	$\nu_{\max} (^{29}\text{Si})$	$\nu_{\max} (^{30}\text{Si})$
LO + TA	566	566.4	569.1	559	548.1
TO + TA	610	610.8	612	601.6	591.5
LO + LA	739	739.1	741	728.3	715.6
TO + LA	819	819	817.8	804.3	791
TO + LO	886	~ 888	~ 890	873.5	859
TO + TO	960	~ 959	~ 962	944	930
2TO + TA	1118	1119	1122.4	(*)	(*)
2TO + LO	1299	1299.5	~ 1302	1278.3	1253.5
3TO	1448	1448.8	~ 1450	1425.1	1398.6

(*) Not determined because of high concentration of oxygen in sample. Error in the determination of phonon peak does not exceed 0.3 cm^{-1} .

3.1.1. IR spectrum of carbon. The band of optical absorption at 605 cm^{-1} (300 K), and 607 cm^{-1} (16 K) is due to LVM of $^{\text{nat}}\text{Si-C}_s$ group with participation of the atoms of Si of natural isotopic composition having a full width at half maximum (FWHM) $\sim 6\text{ cm}^{-1}$ at 300 K and $\sim 3\text{ cm}^{-1}$ below 80 K [6,8]. Thus, for its measurement a spectral resolution of 0.5 cm^{-1} is sufficient. However a real problem is the fact that the Si-C band is just situated at the top of the strongest intrinsic absorption of Si which is a combined absorption band of transverse optical (TO) and acoustic (TA) phonon at 610 cm^{-1} (Table 2).

Fig.1 gives the absorption spectrum of carbon impurities in sample 4 (Table 1), obtained after subtraction of the spectrum of a sample with an ultimately low content of carbon. The carbon content N_C (cm^{-3}) is found from a known relation:

$$N_C = \alpha_C K_C, \quad (1)$$

where α_C is the experimentally determinable absorption coefficient, K_C is the calibration coefficient. According to the standard [8] the values for calibration coefficients in case of carbon are equal to $8.2 \cdot 10^{16}$ and $3.7 \cdot 10^{16}$ at/cm^2 at $T = 300\text{ K}$ and at $T < 80\text{ K}$, respectively.

The results for the determination of carbon impurities in the investigated samples of poly-isotopic Si are given in Table 1. The correlation between the data of both laboratories as well as with passport data („certified values“) is given.

3.1.2. IR spectra of oxygen. As it was already pointed out, the most intensive band, corresponding to the impurity of oxygen in Si of natural isotopic composition, is close to 1107 cm^{-1} at room temperature and has a FWHM of about 32 cm^{-1} . It refers to an asymmetrical stretching vibration of the $^{\text{nat}}\text{Si-}^{16}\text{O-}^{\text{nat}}\text{Si}$ quasi-molecule and overlaps with the intrinsic absorption band of silicon lattice comprising a combination of a transverse optical phonon and a transverse acoustic phonon with the center at 1118 cm^{-1} and a FWHM of about 50 cm^{-1} at room

temperature (Table 2). The content of oxygen in $^{\text{nat}}\text{Si}$ is determined by a relation similar to (1) including the calibration coefficient K_O for oxygen which amounts $3.14 \cdot 10^{17}$ at/cm^2 according to [7] (in [14] a close value of $3.07 \cdot 10^{17}$ at/cm^2 is given). The oxygen band shows a complex temperature behavior. At low temperatures near 5 K the broad room temperature band at 1107 cm^{-1} is removed by a relatively narrow band at 1136 cm^{-1} and two smaller band components at 1134 , 1132 cm^{-1} (Fig. 2). These three band components correspond to the isotopic LVM of the Si-O groups $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$, $^{28}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ and $^{28}\text{Si-}^{16}\text{O-}^{30}\text{Si}$.

For measurements at low temperatures the influence of the lattice (phonon) absorption in this region is not significant since, as it can be seen from Fig. 2, a narrow band of asymmetric stretching vibrations of quasi-molecule Si-O-Si is located in the range of maximum of much less intensive combination $2\text{TO} + \text{TA}$ band (absorption coefficient is equal to $\sim 0.345\text{ cm}^{-1}$ $T = 7\text{ K}$ [15]).

In general the calibration coefficient K_O of the band centered at 1136.4 cm^{-1} in temperature range of $17 < T < 50\text{ K}$ depends upon temperature, spectral resolu-

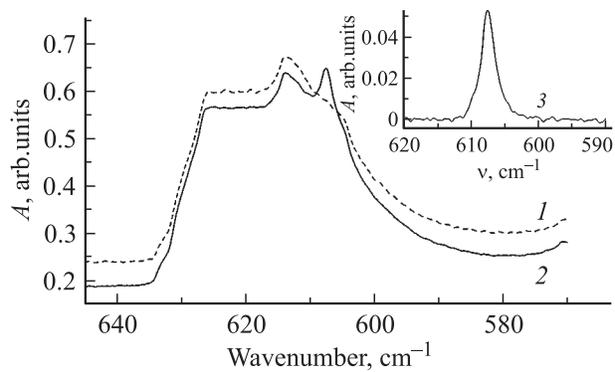


Figure 1. Absorption spectra of $^{\text{nat}}\text{Si}$ at 607 cm^{-1} ($T = 17\text{ K}$): 1 — sample 1, 2 — sample 4, 3 — absorption band of Si- ^{12}C complex in sample 4. Numeration of samples corresponds to Table 1.

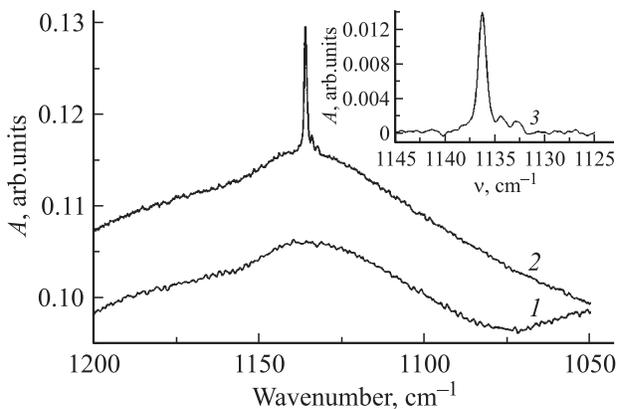


Figure 2. Absorption spectra of the $^{\text{nat}}\text{Si}$ at 1136 cm^{-1} ($T = 17\text{ K}$): 1 — sample 1, 2 — sample 4, 3 — absorption band of Si- ^{16}O -Si quasi-molecule in sample 4. Numeration of samples corresponds to Table 1.

tion, and the selected apodization function. However, as it was shown in [16,17], at $T < 17$ K the value of K_O actually does not depend upon temperature but only upon resolution and apodization function [4]. Thus, at 8 K and at resolution of 0.3 cm^{-1} , it is equal to $1.05 \cdot 10^{16} \text{ at/cm}^2$ [4]. While determining the impurity of oxygen in natural and mono-isotopic (see below) Si we used the value of $K_O = 1.23 \cdot 10^{16} \text{ at/cm}^2$ estimated for the series of silicon samples with various content of oxygen and registered with spectral resolution of 0.5 cm^{-1} at $T = 17$ K (IChHPS) and $T = 5$ K (PTB). The coefficient $K_O = 1.23 \cdot 10^{16} \text{ at/cm}^2$ has been derived by means of measurements of the same material at low and at room temperature and the use of the generally accepted value of $K_O = 3.14 \cdot 10^{16} \text{ at/cm}^2$ for the calculation of the oxygen content from the room temperature spectrum. The used sample thickness were 3 cm for the 393 K and 0.3 cm for the 5 K measurement.

3.2. IR absorption spectra of C and O in samples of mono-isotopic silicon

3.2.1. Phonon spectra of samples ^{28}Si , ^{29}Si and ^{30}Si . It follows from the previous section that in order to provide an adequate description of the absorption bands of the carbon and oxygen impurities in silicon with natural composition the data are required on lattice vibrations, i.e. on spectral position and on intensity of different phonon modes observed in the absorption range of the stated impurities. At going to isotopically enriched samples alongside with the averaged lattice mass change both the phonon spectrum of the matrix, and position of $\text{Si-}^{16}\text{O-Si}$ and $\text{Si-}^{12}\text{C}$ quasi-molecule bands, comprising the silicon atoms of the given isotops should be changed.

Fig. 3 gives the experimental phonon spectra for mono-isotopic ^{28}Si , ^{29}Si , ^{30}Si and for natSi at room temperature in the range 1200 and 600 cm^{-1} . It can be seen that the absorption bands of ^{28}Si , lattice are shifted to higher frequencies with respect to the phonon spectrum of natSi

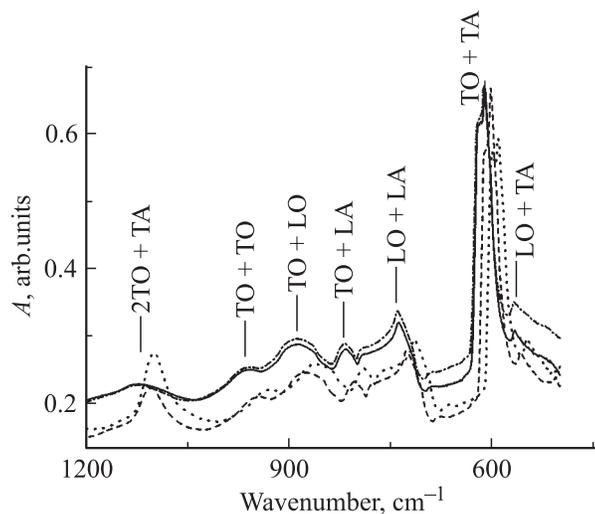


Figure 3. Phonon spectra of mono-isotopic ^{28}Si , ^{29}Si , ^{30}Si and natSi composition in the range $1200\text{--}500 \text{ cm}^{-1}$ at $T = 300$ K.

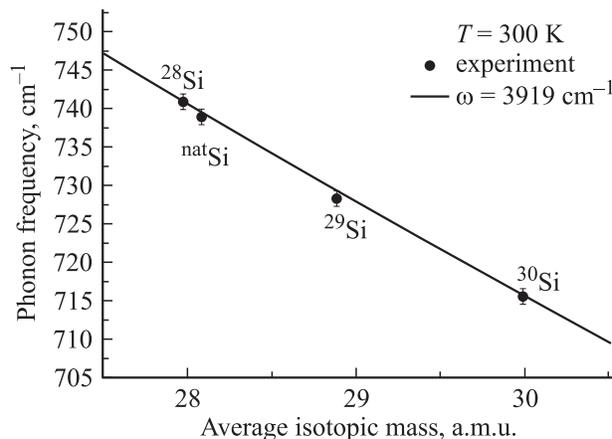


Figure 4. LO + LA phonon frequencies as function of average nuclear mass in samples of various isotopic composition of Si including natSi ($T = 300$ K).

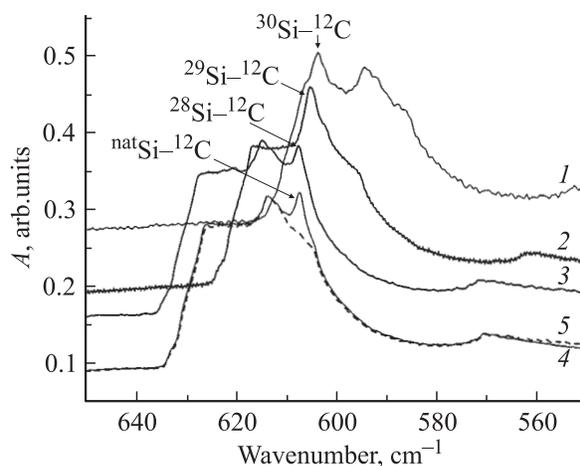


Figure 5. Absorption spectrum of TO + TA phonons and Si-C complex in silicon samples of various isotopic composition ($T = 17$ K): 1 — sample Si30-2-Pr8-part2, 2 — sample Si29-2-Pr8-part2, 3 — sample Si28-4-Pr10, 4 — sample 4, 5 — sample 1. Numeration of samples corresponds to Table 4 and Table 1.

and the corresponding bands of isotopic ^{30}Si and ^{29}Si are shifted to the opposite frequency direction according to the well-known relation between the frequency of phonon $\omega(k)$ and the atomic mass m [18,19]:

$$\omega(k) \propto m^{-1/2}. \tag{2}$$

Table 2 gives the maxima of phonons absorption for Si with different isotopic contents in the stated spectral range at room temperature. The dependence of phonon frequency $\omega(k)$ (with LO + LA phonon as an example) upon the average isotopic atomic mass of Si for the samples with different isotopic composition is given in Fig. 4.

3.2.2. IR spectra of carbon in mono-isotopic silicon. As it was stated above, the absorption band of Si-C groups in the spectrum of natSi is situated at the top of

Table 3. Spectral position ν_{\max} (cm^{-1}) and full width at half-maximum (FWHM) $\Delta\nu_{1/2}$ (cm^{-1}) of absorption bands of Si^{12}C quasi-molecule in IR spectra of silicon with natural isotopic composition $^{\text{nat}}\text{Si}$ and of mono-isotopic Si

T, K	$^{\text{nat}}\text{Si}^{12}\text{C}$		$^{28}\text{Si}^{12}\text{C}$		$^{29}\text{Si}^{12}\text{C}$		$^{30}\text{Si}^{12}\text{C}$	
	ν_{\max}	$\Delta\nu_{1/2}$	ν_{\max}	$\Delta\nu_{1/2}$	ν_{\max}	$\Delta\nu_{1/2}$	ν_{\max}	$\Delta\nu_{1/2}$
300	605*	5.3 ± 0.1	605	**	603.1	**	600.2	**
17	607.4*	2.57 ± 0.03	607.7	2.44 ± 0.04	605.6	2.67 ± 0.06	603.8	2.89 ± 0.11

* 605.0 cm^{-1} , $\Delta\nu_{1/2} = 6 \text{ cm}^{-1}$ at $T = 300 \text{ K}$ [5]; 607.5 cm^{-1} , $\Delta\nu_{1/2} = 3 \text{ cm}^{-1}$ at $T < 80 \text{ K}$ [5].

** Not determined because of great error of bands separation.

Table 4. Concentration (cm^{-3}) of oxygen and carbon impurities in mono-isotopic silicon according to IR inter-laboratory determination

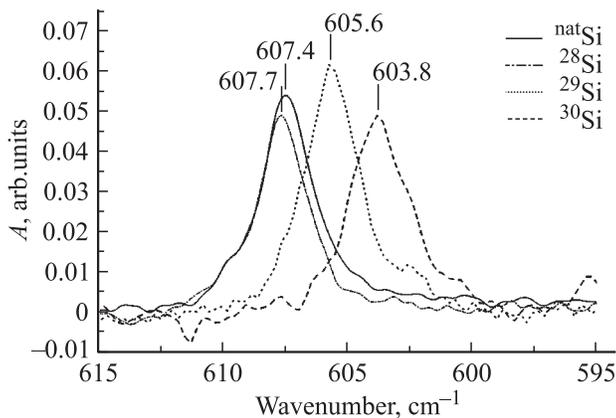
Designation of sample according to SIC (thickness, mm)*	Oxygen		Carbon	
	IChHPS, $T = 300 \text{ K}$	PTB, $T = 5 \text{ K}$	IChHPS, $T = 300 \text{ K}$	PTB, $T = 5 \text{ K}$
Si28-4-Pr10 (1.66)	$(3.2 \pm 0.5) \cdot 10^{16}$	$(4 \pm 0.4) \cdot 10^{16}$	$(2.8 \pm 1.4) \cdot 10^{16}$	$(1.4 \pm 0.1) \cdot 10^{16}$
Si28-3-Pr10 (2.18)	$\leq 8 \cdot 10^{15}$	$(3.3 \pm 0.1) \cdot 10^{14}$	$\leq 5 \cdot 10^{15}$	$(1.6 \pm 1.0) \cdot 10^{15}$
Si28-6.1-Pr10-part4 (2.18)	$(2.3 \pm 0.4) \cdot 10^{17}$	$(2.0 \pm 0.2) \cdot 10^{17}$	$(3.7 \pm 0.2) \cdot 10^{16}$	$(3.3 \pm 0.4) \cdot 10^{16}$
Si29-2-Pr8-part2 (2.33)	$(3.1 \pm 0.8) \cdot 10^{17}$	**	$(5 \pm 1) \cdot 10^{16}$	**
Si30-2-Pr8-part2 (1.78)	$(5.6 \pm 0.6) \cdot 10^{17}$	**	$(4 \pm 1.5) \cdot 10^{16}$	$(4.6 \pm 0.1) \cdot 10^{16}$

* Sample Identification Code (SIC): isotope—number of charge—number of product (10 — FZ single crystal, 8 — Cz single crystal) — number of studied part of the crystal according to cutting scheme. For samples in the 1 and 2 lines of the Table 4 the number of studied part of crystal is not determined.

** Not determined because of high concentration of oxygen and carbon in the sample (full absorption).

the strongest phonon absorption of Si. The same situation is also observed in case of enriched Si, as it is seen from Fig. 5 where the composite band near 610 cm^{-1} shifts with respect to the same band in $^{\text{nat}}\text{Si}$ according to (2). Due to the fact that the samples with different isotopic composition and with the content of carbon lower than the limit of detection of IR spectroscopic method were not available ($\sim 5 \cdot 10^{14} \text{ cm}^{-3}$) [8], it was, strictly speaking, impossible to isolate the absorption band of carbon from composite bands shown in Fig. 5. Assuming that the band shape of TO + TA phonon band do not change significantly due to the isotop

exchange (though it takes additional experimental testing in future), the phonon band of the sample of natural isotopic composition with carbon content less than $3 \cdot 10^{15} \text{ cm}^{-3}$ on Fig. 1 could be taken for the baseline subtraction. The obtained absorption bands of quasi-molecules $^{28}\text{Si-C}$, $^{29}\text{Si-C}$ and $^{30}\text{Si-C}$ are given on Fig. 6 and their spectral parameters at 17 K are presented in Table 3. For the determination of carbon in the investigated mono-isotopic samples we used the above-given values for calibration coefficients from [8] at room temperature and below 80 K for the band centered at 607 cm^{-1} . The data obtained are given in Table 4.

**Figure 6.** Absorption spectra of Si^{12}C complex at 600 cm^{-1} ($T = 17 \text{ K}$) in samples of monoisotopic Si and of silicon with natural isotopic composition: ^{30}Si — sample Si30-2-Pr8-part2, ^{29}Si — sample Si29-2-Pr8-part2, ^{28}Si — sample Si28-4-Pr10, $^{\text{nat}}\text{Si}$ — sample 4. Numeration of samples corresponds to Table 4 and Table 1.**Table 5.** Dependence of position ν_{\max} , full width at the half maximum (FWHM) $\Delta\nu_{1/2}$ and intensity of absorption band of $^{28}\text{Si}^{16}\text{O}^{28}\text{Si}$ quasi-molecule in IR spectrum of mono-isotopic silicon ^{28}Si (sample Si28-4-Pr10) on spectral resolution at $T = 17 \text{ K}$ (Happ–Genzel apodization function)

Resolution, cm^{-1}	$\nu_{\max}, \text{cm}^{-1}$	$\Delta\nu_{1/2}, \text{cm}^{-1}$	Intensity, r.u.
0.5	1136.3	$0.81 \pm 0.02^*$	0.32
0.3	—	$0.68 \pm 0.01^*$	0.38
0.2	—	$0.63 \pm 0.01^*$	0.39
0.1	—	$0.59 \pm 0.01^*$	0.40

* FWHM was determined by approximation of band shape with Lorenz function.

3.2.3. IR spectrum of oxygen in mono-isotopic silicon. Table 6 gives the spectral positions and FWHMs at room temperature of the absorption bands of quasi-molecules $^{28}\text{Si}^{16}\text{O}^{28}\text{Si}$, $^{29}\text{Si}^{16}\text{O}^{29}\text{Si}$ and $^{30}\text{Si}^{16}\text{O}^{30}\text{Si}$ for

corresponding samples of mono-isotopic silicon. The small low-frequency shift at practically unchanged half-width is observed.

The oxygen spectra for the samples of mono-isotopic silicon at low temperatures, i.e. below 20 K, are of the greatest interest since, as it is seen from Fig. 2, for the ^{nat}Si an isotopic splitting of the band centered at 1136 cm^{-1} takes place.

Determination of principal spectral parameters (position and FWHM) of the $\text{Si-}^{16}\text{O-Si}$ band at low temperatures in spectra of mono-isotopic silicon calls for their registration at spectral resolution $\lesssim 0.3\text{ cm}^{-1}$ [5]. Fig. 7 demonstrates the $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$ band at 1136.4 cm^{-1} for sample Si28-4-Pr10

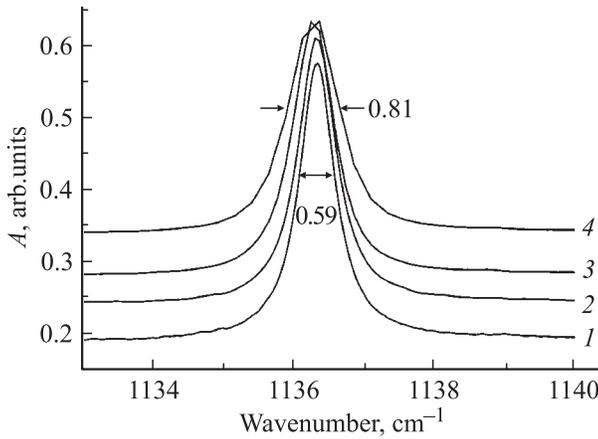


Figure 7. Dependencies of the full width at half maximum (FWHM) of the absorption band of $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$ quasi-molecule in mono-isotopic ^{28}Si (sample Si28-4-Pr10 from Table 4) on spectral resolution ($T = 17\text{ K}$): 1 — 0.1 cm^{-1} , 2 — 0.2 cm^{-1} , 3 — 0.3 cm^{-1} , 4 — 0.5 cm^{-1} .

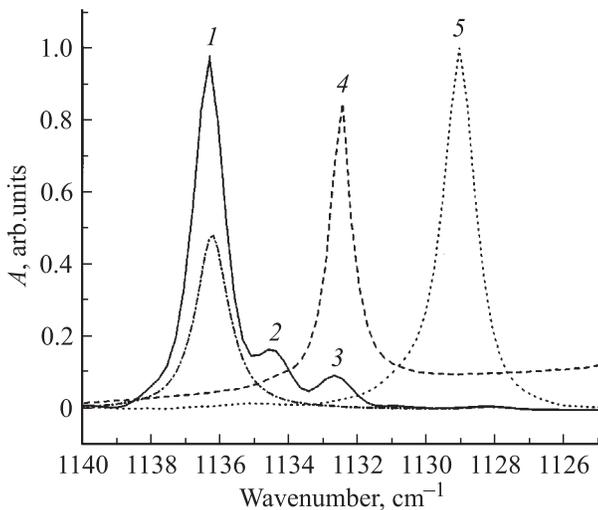


Figure 8. Normalized to thickness spectra of $\text{Si-}^{16}\text{O-Si}$ quasi-molecule at 1130 cm^{-1} ($T = 17\text{ K}$) in mono-isotopic samples Si30-2-Pr8-part2, Si28-6.1-Pr10-part4, Si29-2-Pr8-part2 (Table 4) and in ^{nat}Si , sample 5 (Table 1). 1 — $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$ (1136.4 cm^{-1}), 2 — $^{28}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ (1134.5 cm^{-1}), 3 — $^{28}\text{Si-}^{16}\text{O-}^{30}\text{Si}$ (1132.2 cm^{-1}), 4 — $^{29}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ (1132.5 cm^{-1}), 5 — $^{30}\text{Si-}^{16}\text{O-}^{30}\text{Si}$ (1129.2 cm^{-1}). The last spectrum is twice reduced along ordinate axis.

Table 6. Position ($\nu_{\text{max}},\text{ cm}^{-1}$) and full width at half maximum (FWHM) $\Delta\nu_{1/2}(\text{ cm}^{-1})$ of absorption bands of $\text{Si-}^{16}\text{O-Si}$ quasi-molecules in IR spectra of silicon with natural isotopic composition ^{nat}Si and mono-isotopic silicon at two temperatures

$T, \text{ K}$	$^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$		$^{29}\text{Si-}^{16}\text{O-}^{29}\text{Si}$		$^{30}\text{Si-}^{16}\text{O-}^{30}\text{Si}$	
	ν_{max}	$\Delta\nu_{1/2}$	ν_{max}	$\Delta\nu_{1/2}$	ν_{max}	$\Delta\nu_{1/2}$
300	1107	32 ± 1	1103.1	36 ± 1	1099.3	33 ± 0.5
17	$1136.3^{1)}$	0.60 ± 0.01	$1132.5^{2)}$	(*)	$1128.9^{3)}$	(*)

(*) Not determined because of great concentration of oxygen in the sample.

¹⁾ $\nu_{\text{max}} = 1136.4\text{ cm}^{-1}$ [5]; ²⁾ $\nu_{\text{max}} = 1131.0\text{ cm}^{-1}$ according to theoretical data [20] and $\nu_{\text{max}} = 1132.5\text{ cm}^{-1}$ according to experimental data [13]; ³⁾ $\nu_{\text{max}} = 1125.3\text{ cm}^{-1}$ according to theoretical data [20], $\nu_{\text{max}} = 1129.2\text{ cm}^{-1}$ [22] and $\nu_{\text{max}} = 1129.1\text{ cm}^{-1}$ to experimental data [13].

from Table 4 recorded with four values of spectral resolution. The obtained values of FWHM of this band are given in Table 6. It can be seen that in going from resolution 0.5 cm^{-1} to 0.1 cm^{-1} the FWHM slightly decreases and at further increase of resolution becomes constant and equal to $(0.59 \pm 0.01)\text{ cm}^{-1}$. It is evidence for registration of true shape of this band. This value agrees with FWHM of the same band in spectrum of the ^{nat}Si [5,16,17].

Unfortunately, the registration of true band shapes of $^{29}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ and $^{30}\text{Si-}^{16}\text{O-}^{30}\text{Si}$ quasi-molecules in spectra of ^{29}Si and ^{30}Si was impossible due to high concentration of oxygen in the sample. Even for its minimal thickness (0.9 mm) the total absorption of corresponding bands was observed. That is why Table 6 summarizes only spectral positions of absorption bands of quasi-molecules $\text{Si-}^{16}\text{O-Si}$. It should be noted that, as it was expected, the position of the $^{28}\text{Si-}^{16}\text{O-}^{28}\text{Si}$ band for ^{28}Si coincides with the position of the same band in the spectrum of natural silicon but it does not have low-frequency components corresponding to vibrations of $^{28}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ and $^{28}\text{Si-}^{16}\text{O-}^{30}\text{Si}$. The obtained earlier theoretically in [20,21] and experimentally determined in [13] spectral position of the $^{29}\text{Si-}^{16}\text{O-}^{29}\text{Si}$ band agrees satisfactorily with the experimental value for ^{29}Si obtained in this study (Table 6). The spectral position of $^{30}\text{Si-}^{16}\text{O-}^{30}\text{Si}$ band was determined earlier in [22] from spectrum of ^{nat}Si but containing $\sim 3 \cdot 10^{17}\text{ cm}^{-3}$ of oxygen, as well as in isotopically enriched ^{30}Si [13]. It can be seen from Table 6 that these values are very close to the experimental one obtained here for ^{30}Si and is by 3.6 cm^{-1} higher as compared with the predicted value [20]. The isotopic shift of oxygen bands of ^{28}Si and of ^{29}Si amounts 3.8 cm^{-1} just as the shift of the oxygen bands of ^{29}Si and of ^{30}Si . The isotopic shift, theoretically predicted in [20,21], was slightly greater and equal to 5.3 cm^{-1} that can be probably explained by theoretical model fallibility that does not consider influence of nearest and extended silicon atoms. It should be noted that the vibrational frequencies of the Si-O-Si molecule (for all isotopic species) predicted recently according to improved multi-atom model in [13] are very close to experimental values.

Fig. 8 presents spectra of quasi-molecules Si-¹⁶O-Si at 1130 cm⁻¹ ($T = 17$ K) for samples Si30-2-Pr8-part2, Si28-6.1-Pr10-part4, Si29-2-Pr8-part2 and natural silicon sample 5 from Table 1, normalized to thickness, and evidently demonstrates the isotopic shift of antisymmetric stretching vibration band of quasi-molecule Si-¹⁶O-Si while going from silicon of natural isotopic composition to mono-isotopic samples.

Actually there is no difference between the quantitative determination of oxygen content in ²⁸Si and in natural silicon.

As for ²⁹Si and ³⁰Si isotopes, due to absence for known reasons of calibration coefficients for ²⁹Si-¹⁶O-²⁹Si and ³⁰Si-¹⁶O-³⁰Si bands and assuming that their band shape does not differ strongly from the shape of ²⁸Si-¹⁶O-²⁸Si band in natural silicon we also used the calibration coefficient of ²⁸Si-¹⁶O-²⁸Si band in natural silicon equal to $1.23 \cdot 10^{16}$ cm⁻² for determination of oxygen in ²⁹Si and ³⁰Si (for resolution 0.5 cm⁻¹, $T = 17$ K and 5.2 K). The results found for oxygen concentration in all studied samples are given in Table 4.

As it can be seen from above presented results, generalization of IR spectroscopy methods for determination of carbon and oxygen to mono-isotopic silicon, elaborated for natural silicon, can be done at the moment only by taking into account some limitations and assumptions. The possible errors of determination are apparently minimal for ²⁸Si but can be considerable for ²⁹Si and ³⁰Si. For development of a completely well founded IR method for determination of carbon and oxygen impurities in mono-isotopic silicon a study of IR spectra of high-purity samples (in relation to carbon and oxygen with the content of about 10¹⁴ cm⁻³) of mono-isotopic silicon are required first of all. These samples could be used as the reference samples. For each isotope a series of samples with the known content of C and O estimated by independent method for determination of calibration coefficient in relationship (1) is also strongly needed.

4. Conclusions

1. The IR spectra of all three silicon isotopes in the form of bulk single crystals (²⁸Si with enrichment more as 99.9%, ²⁹Si and ³⁰Si with enrichment more than 90%) has been studied at $T = 300$, 17 and 5 K in spectral range 550–1200 cm⁻¹ which refers to absorption of Si-¹⁶O-Si and Si-¹²C group. The spectral position of phonon maximum at 300 K have been determined.

2. The spectral features of the Si-¹²C band centered at 605 cm⁻¹ for all silicon isotopes in comparison with silicon of natural isotopic composition as well as its isotopic shift at 300 and 17 K have been determined.

3. The spectral position of Si-¹⁶O-Si band in region of 1136 cm⁻¹ for all silicon isotopes in comparison with silicon of natural isotopic composition as well as its isotopic shift at 300 and 17 K has been determined. The dependence of shape of asymmetric stretching vibration band of quasi-molecule ²⁸Si-¹⁶O-²⁸Si in spectrum of ²⁸Si on spectral

resolution has been studied. Its full width at half maximum height equal to 0.6 cm⁻¹ agrees with the value for the natural silicon.

4. The perspectives of generalization of IR spectroscopy method for determination of carbon and oxygen impurities in silicon of natural isotopic composition to mono-isotopic silicon have been discussed. The content of C and O impurities in ²⁸Si, ²⁹Si and ³⁰Si single crystals has been estimated. It was shown that the content of carbon and oxygen in the studied samples of ²⁸Si and of carbon in ²⁹Si and ³⁰Si is $\sim 10^{16}$ cm⁻³ on average. The content of oxygen in ³⁰Si is by an order of magnitude greater.

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