



Diagnostics of impurity composition of high-purity monosilane by results of the analysis of a test silicon single crystal[☆]

Vladimir A. Gavva^{a,b}, Anatolii V. Gusev^{a,b}, Tatiana V. Kotereva^{a,*}

^a *Devyatykh Institute of Chemistry of High Purity Substances, Russian Academy of Sciences, 49 Tropinina Str., Nizhny Novgorod 603950, Russia*

^b *Lobachevsky State University of Nizhny Novgorod, 23 Prospekt Gagarina, Nizhny Novgorod 603950, Russia*

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ABSTRACT

Elements the 3 and 5 of groups of the Periodic System and carbon are the most important impurities in silicon. The estimation technique of carbon, boron and phosphorus impurity content in high-purity monosilane has been proposed. The technique involves the preparation of polycrystalline silicon by silane decomposition, growing a test single crystal by the floating zone melting method and analysis of single crystal samples by IR spectroscopy. Calculation of impurity concentration in polycrystalline silicon has been performed using results on their content in the test single crystal samples, data on impurity distribution in the liquid-solid system and sample coordinates along the ingot length. Effective impurity distribution coefficients in the solid-liquid system for specific growing conditions have been calculated using the Burton-Prim-Slichter equation. Results for the test silicon samples with natural isotopic composition and ²⁸Si isotope enriched ones obtained from monosilane samples with different impurity contents have been reported. Results on IR spectroscopic studies of impurity composition for the test silicon single crystal are in agreement with the concentration data obtained by chromatography. The concentration of 3 and 5 group impurities in monosilane were in the range 4×10^{-9} – 2×10^{-6} at. %, and for carbon concentration was 2×10^{-6} – 6×10^{-4} at.%. The measurement uncertainty by IR spectroscopy does not exceed 15% for carbon impurity and 20% for boron and phosphorus. We show that the upper limit of carbon content in monosilane detected using this method is determined by its solubility in silicon, while the bottom limit depends on the detection accuracy of the IR spectroscopy technique and possible background contamination.

1. Introduction

Silane technology is widely used for the synthesis of high purity semiconductor silicon [1,2]. The most important impurities in silicon are 3 and 5 group elements the content of which determines its electrophysical properties, i.e. conductivity type and electrical resistivity. The quality of single crystal semiconductor silicon depends largely on carbon impurity content. Carbon is not an electrically active impurity but its high content produces structural defects in single crystals. Carbon content in electronic grade semiconductor silicon should not exceed 100 ppb and the concentration of electrically active impurities such as boron, arsenic, phosphorus and others should be less than 1 ppb [3]. Semiconductor silicon parameters are mainly determined by the concentration of these impurities in monosilane. Therefore monosilane impurity composition control is important.

Impurity content in monosilane can be assessed using IR spectroscopy, gas chromatography, chromatographic mass spectroscopy but

the detection limits of these techniques are insufficient for high purity monosilane analysis [4,5]. Known is a test method of characterizing SiH₄ and other silicon containing precursors based on the deposition of epitaxial silicon layers and measurement of their electrophysical parameters for assessing the content of electrically active impurities [3]. However, that method does not allow identifying the impurities, does not allow for impurity compensation and does not provide carbon concentration information. The chemical purity of monosilane can be characterized by the impurity composition of polycrystalline silicon deposited from it, but direct characterization of carbon and electrically active impurities in polycrystalline silicon is complicated due to the absence of reliable and sensitive analytical methods. The aim of this work is to develop a method for the diagnostics of SiH₄ impurity composition by analyzing impurity content in a test single crystal grown from the polycrystalline specimen.

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* Corresponding author.

E-mail addresses: gavva@ihps.nnov.ru (V.A. Gavva), gusev@ihps.nnov.ru (A.V. Gusev), kotereva@ihps.nnov.ru (T.V. Kotereva).

2. Experimental

The concentration of carbon and 3 and 5 group elements in single crystal silicon can be determined with a high sensitivity using absorption IR spectroscopy. Results obtained for single crystal material are used for calculating impurity contents in the source polycrystal. Analysis of low weight test silicon specimens obtained from a monosilane sample allows saving raw materials, promptly modifying process parameters and adding more purification stages where necessary.

The impurity composition analysis technique includes the following stages:

- obtaining polycrystalline silicon in heterogeneous monosilane decomposition reaction;
- growth of a test single crystal using one-pass zone melting;
- cutting of planar silicon specimens for analysis from different parts along the ingot length;
- IR spectroscopy analysis of single crystal specimens;
- calculation of impurity concentrations in the test polycrystalline based on test single crystal analysis data.

A single crystal silicon specimen was obtained by thermal decomposition of monosilane in a cooled wall metallic reactor. Polycrystalline silicon was deposited onto 4–5 mm diam. rod shaped silicon substrate electrically heated to 800 °C. The rod was preliminarily weighed and analyzed with IR spectroscopy. Monosilane was decomposed at 0.105 MPa (abs.). The resultant polycrystals were in the form of ~10 mm diam. cylinders weighing approx. 20 g. We used silane and silicon samples having the natural isotope composition and isotope enriched samples with a main ²⁸Si isotope content of more than 99.99% [6]. Impurity distributions in isotope enriched silicon as determined using IR spectroscopy were described by us earlier [7,8].

The polycrystalline sample was removed from the reactor, weighed and zone melt grown to single crystal. The polycrystal surface was not treated before the growth. The test single crystal was grown in a high purity argon flow (TU 6–21–12–94) with a carbon impurity content of < 1x10⁻⁶ vol.%. The growth rate was 2 mm/min. The single crystals had the (100) or (111) orientations. After that we cut specimens for analysis in the form of 1–3 mm thick planar plates from different parts along single crystal length.

Silicon absorption spectra in the 200–700 cm⁻¹ range were recorded on a Bruker IFS113v Fourier spectrometer with MCT and DTGS detectors and polyethylene windows; for measurements in the 400–2000 cm⁻¹ range we used a KBr beam splitter, and for the 250–700 cm⁻¹ range, a 3.5 μm LAVSAN film. Measurements at helium temperatures were carried out in a closed circuit cryostat with KRS-5 optical windows. We determined the concentrations of carbon and electrically active impurities from IR absorption spectra using calibration coefficients for silicon [9,10]. The measurement uncertainty by IR spectroscopy did not exceed 15% for carbon impurity and 20% for boron and phosphorus.

Impurity concentrations in the source polycrystals were calculated based on the results on their content in the test single crystal specimens, impurity distribution coefficients in the solid-liquid system, sample coordinates along the ingot length and the Pfann equation [11]:

$$\frac{C}{C_0} = 1 - (1 - k_{\text{eff}}) \exp\left(-\frac{k_{\text{eff}}x}{L}\right), \quad (1)$$

where C is the impurity concentration at the point x , C_0 is the initial impurity concentration, k_{eff} is the effective impurity distribution coefficient in the solid-liquid system, x is the coordinate along the ingot length and L is the molten zone length.

Effective impurity distribution coefficients in the solid-liquid system for specific growing conditions were calculated using the Burton–Prim–Slichter equation [12]:

$$k_{\text{eff}} = \frac{k_0}{k_0 + (1 - k_0) \exp(-V\delta/D)}, \quad (2)$$

where k_0 is the effective distribution coefficient, V is the crystal growth rate, δ is the diffusion layer thickness ($1.6D^{1/3}v^{1/6}(2\pi n)^{-1/2}$), D is the impurity diffusion coefficient in the melt, v is the kinematic viscosity of silicon melt ($v = 3.5 \times 10^{-7}$ m²/s) and n is the crystal rotation speed during growth, rad/s.

For the calculations we used equilibrium distribution coefficients k_0 for carbon, boron, phosphorus and arsenic impurities borrowed from [13]. The impurity diffusion coefficients in the melt were borrowed from [14]. k_{eff} calculated using Eq. (2) were 0.113, 0.84, 0.43 and 0.36 for C, B, P and As, respectively.

Impurity concentrations in polycrystal deposited from monosilane were calculated taking into account the rod substrate contribution using the formula

$$C_i^0 = \frac{C_i m_t - C_{rs} m_{rs}}{m_t - m_{rs}}, \quad (3)$$

where C_i^0 is the impurity concentration in polycrystal deposited from monosilane, C_i is the impurity concentration in the polycrystal with the rod substrate calculated from the results on the single crystal, C_{rs} is the impurity concentration in the rod substrate, m_t is the total weight of polycrystal deposited from monosilane and the rod substrate and m_{rs} is the weight of the rod substrate.

3. Results and discussion

3.1. Determination of boron, phosphorus and arsenic impurity contents

High purity monosilane contains boron, phosphorus and arsenic impurities mainly in the form of hybrids, i.e. diborane, phosphine and arsine, respectively. In all the test specimens the arsine and phosphine concentrations as determined using chromatographic mass spectroscopy were within 1x10⁻⁶ vol.% which corresponds to silicon and arsenic concentrations in silicon of less than 5x10⁴ at/cm³. Boron impurity content characterization using chromatographic techniques is complicated due to the high probability of hydrolysis of boron containing impurities during analysis.

Results on boron, phosphorus and arsenic impurity contents in the source polycrystal as determined from the contents of these impurities in the test single crystals are shown in Table 1.

The phosphorus concentration distribution (Fig. 1) agrees well with the data calculated using Eq. (1). This testifies to the absence of the supply of this impurity from the material of the equipment during test specimen growth.

3.2. Determination of carbon impurity content

We analyzed silicon specimens grown from different monosilane batches. Results on carbon concentration in the source polycrystals calculated from the content of this impurity in specimens cut from the test single crystals are shown in Table 2.

Depending on monosilane batch, carbon impurity content in polycrystals varied from 10¹⁵ to 10¹⁷ at/cm³ (see Table 2).

Carbon impurity in monosilane is present mainly in the form of C₁–C₄ hydrocarbons. Hydrocarbon impurity contents as determined using

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