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Isotopic heterogeneity in synthetic and natural silicon carbide

A.A. Shiryaev^a, M. Wiedenbeck^b, V. Reutsky^c, V.B. Polyakov^d, N.N. Mel'nik^e, A.A. Lebedev^f and R. Yakimova^g

^aShubnikov Institute of Crystallography RAS, Leninsky pr. 59, 119333 Moscow, Russia
^bGeoForschungsZentrum, Telegrafenberg, 14473 Potsdam, Germany
^cInstitute of Geology and Mineralogy, SB RAS, pr. Ak.Koptyuga 3, 630090 Novossibirsk, Russia
^dInstitute of Experimental Mineralogy RAS, Chernogolovka, Russia
^eLebedev Physics Institute RAS, Leninsky pr. 53, Moscow, Russia
^fIoffe Physico-Technical Institute RAS, 194021 Sankt Petersburg, Russia
^gLinkoping University, 58183 Linkoping, Sweden

Abstract

The distribution of both carbon and silicon isotopes in synthetic sublimation growth SiC wafers and in natural SiC grains was studied using secondary ion mass-spectrometry (SIMS). Significant variations in both isotopic ratios were observed which were broadly correlated with the crystalline perfection as documented by Raman microspectroscopy. Domains consisting of 15R (or with its admixture) are, on average, enriched in ¹²C isotope relative to 6H domains, and they also show larger scatter in their observed silicon isotope ratios. We ascribe such heterogeneity to fluctuations of Si/C ratio in the growth medium and it is possible to model the spatial extent of such fluctuations. For the natural SiC grains the isotopic data suggest that they grew under relatively stable conditions, although some of them show significant isotopic zoning.

Keywords: A. Inorganic compounds; B. Crystal growth; C. Raman spectroscopy

1. Introduction

Silicon carbide is a material of significant interest for various fundamental and applied fields: from high-power electronics to crystallography and problems of the Earth mantle oxidation state. From the scientific points of view one of the most interesting features of SiC is its ability to form numerous polytypes, i.e. structural modifications, each of which may be regarded as built through the stacking layers of (nearly) identical structure and composition, wherein different crystallographic types differ only in their stacking sequence [1]. The most common polytypes are hexagonal 4H and 6H; rhombohedral 15R and the cubic 3C. In the Ramsdell notation used in this paper to indicate the polytype, the figure indicates number of non-equivalent layers and the letter type of lattice packing: cubic, hexagonal or rhombohedral. Though many physical properties (hardness, thermal conductivity, thermal capacity, etc.) of the polytypes are fairly similar, some important differences do exist, e.g., the band gap varies from 2.4 eV in 3C to 3.23 eV in 2H. Such variations in properties are partly due to various coordinations of Si and C atoms in polytypes, which induce differences in the electronic structure. The simultaneous presence of several polytypes in a single SiC wafer is usually detrimental for technological applications. Pressure and temperature during crystal growth both play important roles determining which polytype is produced [2]. It has also been suggested that impurities and intrinsic defects may influence the stability of polytypes ([3-5] and references therein). Additional information contributing to the understanding of polytypes formation is of considerable applied and basic interest.

Besides its significance in the field of solid state physics, studies of SiC are valuable for geosciences and astrophysics. Silicon carbide occurs in nature as the rather rare mineral moissanite. Numerous finds of moissanite grains in heavy fractions of kimberlites, high-grade metamorphic and mantle derived rocks (for a review see [6]) as well as in meteorites and interstellar dust [7] have already been reported. Since the formation of SiC requires extremely low oxygen fugacity, some geologists consider moissanite as a "geological aberration". However, a growing body of data confirms the rather widespread existence of small SiC grains in various geological settings. Interestingly, carbon isotopic analysis of natural SiC grains always shows that the SiC is enriched in ¹²C carbon [6,8]. The genesis of natural SiC remains a matter for debate [6, 8, 9].

This papers deals with isotopic fractionation related to growth of SiC. Several processes responsible for isotopic fractionation are known [10, 11]. Being a thermodynamic property, equilibrium isotopic fractionation can be expressed in terms of vibrational densities of states (DOS) of substances under consideration via appropriate equations from statistical physics [12, 13]. There are some indications that impurities and intrinsic defects may also influence the degree of the isotope fractionation [14]. Polytypes are interesting for assessing the influence of various lattice imperfections on isotopic fractionation, since polytypes could be represented as stacking faults in regular hexagonal or cubic lattices (e.g., stacking faults in the 3C-SiC are hexagonal polytypes). Importantly, disorder in SiC is not completely random and disordered regions consist of mixture of randomly disordered simple polytype domains and those containing stacking faults distributed periodically or almost periodically. Only few studies have addressed the relationship between isotopic composition and polytypism, one of which documented the dependence of oxygen isotope composition of biotite on relative fraction of polytypes in mica [15].

In the current work, we have used secondary ions mass spectrometry (SIMS) to investigate both carbon and silicon isotopic heterogeneity (ratios ${}^{12}C/{}^{13}C$ and ${}^{28}Si/{}^{29}Si/{}^{30}Si$) in SiC wafers

grown using the sublimation method at very high temperatures as well as in grains of natural moissanite. The main task was to establish the relationship between crystalline quality (polytype and/or disorder) and isotopic composition of SiC.

2. Experimental

2.1. Samples

In this work samples of natural and synthetic SiC were studied. Natural SiC was represented by grains handpicked from heavy fraction of several Yakutian kimberlites. The grains were 0.3–0.5 mm in size, and represented by flattened hexagons or fragments thereof. The colors of the natural grains varied from transparent to dark violet. Raman microspectroscopy showed that the grains were either hexagonal (6H and 4H) or rhombohedral (15R) polytypes.

Synthetic SiC wafers were grown at Linkoping University using the sublimation method [16] at a temperature of circa 2400 °C; temperature gradients over the 2 in wafer diameter did not exceeded 10–20°. During the growth process some instabilities have occurred, leading to the development of macroscopic (few mm²) domains of different polytype compositions and/or different concentrations of charge carriers. The boundaries between the domains were clearly visible due to different coloration (Fig. 1). Raman microspectroscopy revealed that the synthetic samples studied in this work are represented by hexagonal (6H) and rhombohedral (15R) polytypes with domains of disordered 6H SiC with 15R-like regions. In some samples neighboring domains of different color consisted of the same polytype (6H). These variations in optical properties are due to variable concentration of charge compensating impurities.

2.2. SIMS analytical technique

To assess the isotopic homogeneity of the natural and synthetic SiC samples the Cameca ims 6f SIMS instrument at GeoForschungsZentrum was employed to make mass-spectrometric analyses along straight lines, intersecting visually observed boundaries between polytypes. Prior to SIMS analysis the SiC samples were ultrasonically cleaned in high-purity ethanol, dried at 60 °C in atmosphere and then sputter coated with a high purity, 35 nm thick conductive gold coat. Two different synthetic samples were placed in the SIMS instrument as polished slices of SiC held in sample holders using Ta masks. The three other samples, two pieces from one synthetic wafer and a grain mount consisting of five individual grains of natural SiC, were cast in epoxy and polished flat prior to cleaning and gold coating.

Due to the destructive nature of SIMS, questions may arise concerning analytical artifacts of SiC polytypes that might be induced by differences in sputter rate (so-called "matrix effect"). However, it has been shown both experimentally and theoretically that properties of different SiC polytypes are rather similar in respect of their stability against radiation damage [17]. Therefore, from the point of view of SIMS as an analytical tool, different SiC polytypes would be predicted to behave virtually identically.

Our SIMS analyses employed a 500 pA, 17.5 kV 133 Cs⁺ primary beam focused to ~5 µm on the polished sample surface. A secondary extraction voltage of -7.5 kV was used to which no energy offset was applied to a 50 eV energy bandpass. For C isotopic analyses the instrument was operated at elevated mass resolving power of $M/\Delta M\approx$ 5100, which was adequate to resolve 13 C from the nearby isobaric interference 1 H 12 C. A 20 µm contrast aperture was used in conjunction with a 750 µm field aperture (equivalent to a 60 µm field-of-view). A single analysis, consisting of a 5 min preburn followed by 100 cycles of the peak stepping sequence—mass 11.9 (background, 0.1 s per cycle), ¹²C (2 s), ¹³C (10 s)—lasted 26 min. Due to the relatively high mass resolving power employed, an enhanced magnet control (310,000 bits at the ¹²C mass station) was used and this was recalibrated prior to each analysis. As the samples have an intrinsic electrical conductivity electron flooding was not necessary, thus permitting the electron deflecting magnets to be turned off. Under these conditions a typical ¹²C count rate started at \sim 300 kHz and grew to \sim 400 kHz by the end of the single analysis. A dead time correction for discreet dynode ion counting system of 16 ns was applied to all data. Ion counting based precision values for ($^{13}C/^{12}C$)_{meas} of ±0.4‰ to ±0.5‰ were typical for such measurements, whereas the observed internal precisions were typically around ±0.6‰ (1 σ).



Fig. 1. General view of synthetic SiC wafer and example of SIMS measurement area. Length of the scratch is 0.6 mm.

Silicon isotopic measurements were also conducted on selected grains from the grain mount as well as on one of the synthetic sample. Si analyses were run under conditions similar to those used for C, the exception being a reduced mass resolving power of $M/\Delta M \approx 4900$, which is more than sufficient to resolve all Si species from the isobaric SiH peaks. A single analysis, consisting of a 5 min preburn followed by 100 cycles of the peak stepping sequence—mass 27.9 (background, 0.1 s), ²⁸Si (2 s), ²⁹Si (8 s), ³⁰Si (10 s), lasted for a total of 40 min. Typical ²⁸Si count rates of initially 600 kHz and increasing up to 1 MHz were observed during such analyses. Ion counting-based precision values of $\pm 0.20\%$ were typical for both the ²⁹Si/²⁸Si and ³⁰Si/²⁸Si measured ratios, whereas the observed internal precision were typically around $\pm 0.25\%$ and $\pm 0.45\%$, respectively. This difference between the Poisson-based and observed internal precisions resulted from a reproducible trend towards lighter isotopic values (~2% for ³⁰Si/²⁸Si) seen over the course of single measurements.

Some of the synthetic samples were studied using Cameca ims 1270 at the Ion Probe Facility, Edinburgh. Standardization of these SIMS analyses was achieved by investigation of the SiC grains, whose carbon isotopic composition was measured by conventional mass spectrometry. Since SiC is a refractory material and complete oxidation is hindered by rapid build-up of SiO₂ layer, conventional combustion does not give good results. We have used chemical decomposition process according to reaction SiC+4KOH $+2O_2=2H_2O+K_2CO_3+K_2SiO_3$. Obtained carbonate is easily decomposed by phosphoric acid releasing CO₂ for conventional isotopic composition of synthetic SiC wafers ($\delta^{13}C_{PDB}$) is around -21%.

2.3. Raman microspectroscopy

After the SIMS measurements the SiC polytype at each spot locality was determined using Raman microspectroscopy using Jobyn Yvon U1000 spectrometer using wavelength of 488 nm with beam size of $r 10 \mu m$ in backscattering geometry. The measurements were performed in immediate vicinity of the SIMS spots or in the crater itself. Two spectral regions were found to be important for the current study: "low" wavenumbers (acoustical phonons, FTA mode, 100–250 cm⁻¹), and "high" wavenumbers (optical phonons, FTO mode, 740–810 cm⁻¹).

3. Results

3.1. Raman microspectroscopy

Raman spectroscopy showed that the natural grains are well ordered and that each grain consists of single polytype. Four of the grains belong to 6H and one to 15R polytype. In contrast to the natural samples, the selected synthetic wafers are less perfect. Whereas some analyzed regions of the wafers consist of well-defined polytypes, we found regions of the wafer containing disordered SiC using a 10 μ m probing laser beam. The disorder manifests itself in a broadening and distortion of the Raman peaks as well as the appearance of new features. In many cases disordered regions contain mixture of 6H and 15R polytypes. Representative spectra of two polytypes obtained on one of the synthetic samples are shown in Fig. 2.



Fig. 2. Representative Raman spectra of several spots on one of the SiC wafer. Spectra show variations in crystallographic quality of the different spots.

The shape, symmetry and position of Raman peaks are sensitive to polytype variety, disorder, stresses and density of charge carriers [18-20]. In our synthetic samples the FLO mode (situated between 900 and 1000 cm⁻¹) is broadened towards the high wavenumbers side. This indicates small degree of stress due to extended defects [20], but points to different concentration of electrically active dopants [19].

3.2. Carbon isotopes

Carbon isotopic ratios in five mounted single grains of natural SiC (Fig. 3) were analyzed. Grain #4 was the only one consisting of 15R polytype, whereas the other grains consisted of hexagonal varieties. On every grain two to three SIMS measurements were performed. The data from four of these grains (grains 1, 2, 3 and 5) are consistent with a homogenous population. In contrast, the measured ${}^{13}C/{}^{12}C$ ratio of grain 4 (*n*=3) was 3.5‰ lighter than that observed for the main population. As the external reproducibility of our technique is better than 1‰ (1 σ), we can conclude with a high degree of confidence that the C isotopic composition of grain 4 differs from that of the four other grains that were analyzed.



Fig. 3. Measured carbon isotopic ratios for grains of natural SiC. Error bars correspond to 1σ .

Several profiles were measured on synthetic SiC wafers. Each profile comprised between 9 and 20 points separated by 20–130 μ m and each profile intersected one or more visually observed polytype boundaries. Several representative profiles are shown in Fig. 4. Variations in carbon isotope ratios between domains of a given polytype (6H and 15R) are rather small: an absolute difference in the unweighted means of the two populations does not exceed re 1.5 σ . In line with results obtained for the natural SiC grains, the 15R domain appears to have marginally lighter carbon isotopic composition.



Fig. 4. Measured carbon isotopic ratios for SiC wafers. Error bars correspond to 1σ .

A closer look at the available data shows that the SiC wafers are isotopically heterogeneous on microscopic scale with considerable scatter of ${}^{13}C/{}^{12}C$ values even between points separated by only a few tens of microns. It is important to mention that scatter of ${}^{13}C/{}^{12}C$ ratios obtained on different classes of SIMS instruments (Cameca 6f and 1270) are closely comparable. As a proxy of the crystalline quality we have used ratio of intensities of folded TO modes in Raman spectra. Comparison of Raman spectra of points with significantly different isotopic ratios shows existence of qualitative correlation between crystalline quality of the SiC domain and its isotopic composition (Fig. 5). Isotopic composition of domains of high-quality 6H SiC differs (usually heavier) than that of disordered regions where a 15R admixture is present. The relationship between the spectroscopic and isotopic data is addressed in Discussion section. On several wafers gradual changes in carbon isotopic composition with increasing distance from the interpolytype boundary are observed (the most pronounced trends are shown by Fig. 4b, d).



Fig. 5. Ratio of intensities of various peaks (modes) in Raman spectra versus C and Si isotopic ratios for several studied SiC wafers.

3.3. Silicon isotopes

Silicon isotopic analyses were conducted on three individual natural grains (Fig. 6a). These included analyses of grains 2 and 3 from the dominant population identified previously on the basis of C isotopes and Raman spectra (6H polytype) and also of grain 4 (15R) which yielded a distinctly light C isotope signature. Both 29 Si/ 28 Si and 30 Si/ 28 Si ratios of grain 4 were significantly heavier than those observed for grains 2 and 3 by 1.5‰ and 3.1‰, respectively. No evidence for non-linear mass bias was found, though our method would be sensitive to such an effect only at the r 1% level.



Fig. 6. Silicon isotope ratios for natural SiC grains with corresponding grain numbers (panel A) and for synthetic wafers (panel B). Hatched region indicates values for 15R polytype.

A single Si isotope profile, consisting of 10 individual measurements over a 500 μ m distance, was conducted on one synthetic sample. The profile started at 6H domain, passed through 15R and entered another 6H domain. An absolute differences between the unweighted means of the points belonging to different polytypes of $(2.5\pm1.0)\times10^{-5}$ and $(1.2\pm1.2)\times10^{-5}$ (1 σ) were found for the ²⁹Si/²⁸Si and ³⁰Si/²⁸Si ratios, respectively, with the average value for the 15R polytype appearing to be marginally lighter. Therefore, a small difference between the Si

isotopic compositions of these two SiC polytypes may be present, and this conclusion can be asserted with a higher degree of confidence for the case of ²⁹Si/²⁸Si. Again, no evidence for non-linear mass bias was found (Fig. 6b). As in case of carbon isotopes a qualitative correlation between isotopic ratios and Raman features is observed. Namely, the 6H polytype has better defined Si isotopic composition whereas disordered domains with a detectable 15R admixture are characterized by considerable scatter (see Discussion below).

4. Discussion

Our SIMS isotopic study shows that on average, the rhombohedral 15R SiC polytype has lighter carbon than the hexagonal 6H. This trend is observed for both synthetic SiC wafers and for natural SiC grains. In the case of natural SiC, four out of five analyzed grains were of 6H polytype and their carbon was 3.5‰ heavier than that determined on the single 15R grain (Fig. 3). The 15R grain is also distinct from the 6H grains having heavier silicon isotopic composition (Fig. 6a). Disordered regions of the SiC wafers are characterized by the isotope ratios being noticeably different from spots with well-defined polytype. In the analyzed synthetic sample the most crystallographically ordered spot has the lowest ³⁰Si/²⁸Si.

Several processes could be responsible for the observed isotopic heterogeneity of the SiC samples. It is known that due to quantum nature of isotopic effects their magnitude decreases with temperature. The magnitude of isotopic effect is proportional to the ratio of isotope masses in case of kinetic origin, and approaches zero for equilibrium fractionation. Perhaps the most remarkable result of the current study is the observation of isotopic heterogeneities in crystals grown at extremely high temperature ($r_{\rm e}2400$ °C). Tentative explanation of the observed heterogeneities follows below and we will consider several principal stages in the SiC growth process and relevant properties of polytypes. Since the growth process of natural SiC is presently unknown, the corresponding part of the discussion relates only to the synthetic samples.

Sublimation growth of synthetic SiC is a complex process [21] where several growth-related phenomena are known to play important roles and which could produce isotopic fractionation:

(G1) sublimation of the source material;

(G2) mass transport of vapor species (mostly Si₂C, SiC₂, Si) to the growing crystal;

(G3) nucleation and growth.

Finally, the fractionation may occur due to:

(S1) differences in structure between polytypes.

Since crystal growth is believed to be diffusion limited [22], the effect of isotopic fractionation that might occur during the sublimation process (case G1) is unlikely to be significant due to isotopic exchange during transport of material from the source to the seed.

Case G2 is more complex. *Equilibrium* isotope fractionation reaching observed magnitude of 1.5‰ between the vapor species seems improbable due to the high temperatures that are involved, though kinetic effects cannot be fully discounted.

Variations of crystal growth rate (case G3) may produce isotopic heterogeneity due to kinetic isotopic effects. However, since we consider macroscopically small regions of the SiC wafer on which the surface relief was negligible, the growth rate at the dimensions of our SIMS analysis is virtually constant.

Differences in structure between polytypes may also produce some isotopic fractionation (case S1). Variations in the strength of atomic bonding may lead to isotopic fractionation between phases [11]. According to [23] the mean charge on Si ions depends on hexagonality of SiC polytype. However, these differences are not very significant and potential isotopic effect should be small. The number of non-equivalent lattice sites is also polytype dependent: structure of 15R contains five such nodes in comparison with three in 6H. This fact may open room for intrastructural isotopic fractionation similar to that observed, for example, in malachite and phyllosilicates [24]. However, though the second and third coordination spheres are polytype dependent, the nearest neighbors are identical in all polytypes. Therefore, vibrational properties of polytypes are fairly similar, implying small magnitude of the interpolytype isotopic fractionation. The similarity of vibrational density-of-states (VDOS) of SiC polytypes is manifested in Raman and infra-red spectra [25] and in inelastic X-ray and neutron scattering [26]. Virtually identical VDOS of all studied SiC polytypes and preliminary thermodynamic calculations (Polyakov, unpublished) indicates that at the relevant temperatures equilibrium structure-dependent isotopic fractionation between them should have magnitudes significantly smaller than that observed in our experiments.

Here it is appropriate to recall the main reasons for polytype transformation: Each polytype has certain field of stability on P-T diagram [2]. In our case P-T conditions were fairly constant and should have played only a minor role if any. Simultaneous development of several polytypes could occur due to variations in Si/C ratio in the growth system and due to inhomogeneous impurity incorporation [3, 4]. Si/C ratio in the growth medium is important for at least two main reasons: (a) the composition of polytypes shows slight variations in Si/C ratio [27]; and (b) changes in the concentration of carbon or silicon vacancies influences SiC hexagonality [5, 28]. For example, an increase in carbon vacancies would promote the formation of atomic bonds in cubic nodes. Impurities may influence structure of the valence bands and/or influence bond strengths and lengths, thus changing the relative energies between possible stacking sequences.

The arguments given above suggest that the only process which might have produced the observed relationship between isotopic composition and crystalline quality involves small variations in the isotopic composition of incoming vapor species (kinetic effect in case G2). The presence of domains containing from multiple polytypes clearly points to some local instabilities in vapor flow to the growing crystal. It is highly probable that such fluctuations were accompanied by changes in the Si/C ratio and some concomitant isotopic fractionation. Therefore, we believe that the process leading to formation of disordered SiC lattice has also induced heterogeneities in the isotopic composition of the sample. It is important to mention that very high growth temperatures failed to suppress isotopic heterogeneity.

Several of the studied natural SiC grains also show isotopic heterogeneity. This heterogeneity might be due to growth zonation, since Raman spectra of the grains show that their polytypic composition is rather uniform. This suggestion requires additional study, but it is plausible since different growth zones could have different isotopic composition of parent material. Intergrain variations of carbon isotopic composition of natural SiC have already been reported [6, 8].

Whereas we believe that the principal reason for the observed heterogeneity is growth related, the role of lattice defects cannot be fully discounted. As discussed above we have observed that in several cases the 15R polytype appears to be isotopically lighter than the 6H. This difference may be a consequence of somewhat different P-T fields of stability of these two polytypes, but might just as well reflect variations in concentration of intrinsic and extrinsic defects, stabilizing respective structures.

Observation of gradual changes in carbon isotopic ratios in the vicinity of interpolytype boundaries (Fig. 4b, d) makes it possible to estimate the size of the wafer domain affected by mentioned instabilities. From these graphs one can see that growth instabilities leading to appearance of another polytype affected regions spanning $200-400 \mu m$ from the boundary.

In line with our current results, we suggest that the observed correlation between polytypes and oxygen isotopic composition of natural biotite [15] likely reflects some variations in growth conditions.

5. Conclusions

This work reports a detailed investigation of carbon and silicon isotope distributions in the vicinity of interpolytype boundaries in sublimation growth SiC wafers. Significant fluctuations of isotopic ratios (up to 3‰) are observed at the 20–50 micron scale. Raman microspectroscopy shows existence of a broad correlation between perfection of crystalline lattice and its isotopic composition. Namely, domains consisting of pure 6H polytype are, on average, enriched in ¹³C in comparison with domains with an admixture of 15R polytype. The 6H domains also show less variability in Si isotope ratios.

We believe that the observed heterogeneity is explained by a kinetic effect, which is closely related to local variations in Si/C ratio in incoming gas which gave rise to variations different polytypes and also produce isotopic heterogeneities. We have found that gradual changes of isotopic ratios span distances reaching 200–400 μ m from the interpolytype boundary. The extent of such non-uniformities reflects the size of the growth instabilities mentioned above.

Investigation of natural SiC grains suggests that growth process of silicon carbide in nature occur under relatively stable conditions. Several grains show isotopic heterogeneity, which likely reflects growth zonation. In line with results obtained for synthetic SiC wafers, natural grains belonging to 15R polytype were found to differ from 6H grains.

In some sense rare isotopes (e.g., ¹³C) may be considered as isomorphic impurities. This study shows that investigation of heterogeneities of isotope composition may complement studies of impurity distribution in reconstruction of growth processes. Use of isotope ratios looks especially promising for investigation of high-purity materials with low concentration of extrinsic defects.

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