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Diffusion-driven precipitate growth and ripening of oxygen precipitates in boron doped silicon by dynamical x-ray diffraction

J. Will,^{1,a)} A. Gröschel,¹ C. Bergmann,¹ E. Spiecker,² and A. Magerl¹

¹*Crystallography and Structural Physics, University of Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen, Germany*

²*Center for Nanoanalysis and Electron Microscopy, University of Erlangen-Nürnberg, Cauerstr. 6, 91058 Erlangen, Germany*

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X-ray Pendellösung fringes from three silicon single crystals measured at 900 °C are analyzed with respect to density and size of oxygen precipitates within a diffusion-driven growth model and compared with TEM investigations. It appears that boron doped (p+) material shows a higher precipitate density and a higher strain than moderately (p-) boron crystals. *In-situ* diffraction reveals a diffusion-driven precipitate growth followed by a second growth regime in both materials. An interpretation of the second growth regime in terms of Ostwald ripening yields surface energy values (around 70 erg/cm²) similar to published data. Further, an increased nucleation rate by a factor of ~13 is found in the p+ sample as compared to a p- sample at a nucleation temperature of 450 °C.

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I. INTRODUCTION

During silicon (Si) crystal growth by the Czochralski method oxygen (O) is incorporated into the material from the quartz crucible via the melt. This binary component system of O in Si becomes thermodynamically a supersaturated solution during cooling. It will eventually form a second phase of SiO_x precipitates during subsequent thermal heat treatments below the solubility limit.¹ The precipitated phase causes strain fields in the host lattice and this serves as a sink for unintentionally introduced metallic impurities in the Si lattice in particular during device fabrication. This process is well known as internal gettering. Related to this functionality, it is crucial to have control over the density, size, and morphology of the precipitates. Diffraction techniques^{2,3} and in particular dynamical X-ray diffraction expressed by Pendellösung fringes⁴⁻⁶ are highly sensitive to the volume misfit between the precipitated phase and the host lattice, which is the origin of the strain fields. As an additional benefit, these techniques are capable of *in-situ* experiments at high temperature, which allows the monitoring of the entire precipitation kinetics.

The growth kinetics at temperatures above 750 °C is well understood within a diffusion-driven growth model⁷ in moderately doped material where the doping content is low compared to the O concentration. However, the normal diffusivity⁸ becomes enhanced at temperatures below 750 °C,⁹⁻¹² which influences both the nucleation and the growth kinetics in this temperature regime. While it is widely accepted, that fast diffusing O dimers cause this enhanced O diffusion, literature data show a wide spread of diffusion constants up to several orders of magnitude. In highly doped material with dopant concentrations exceeding the O concentration by about one order of magnitude, the precipitation behavior changes again as function of the

dopant, the dopant concentration, and the temperature. For highly boron (B) doped (p+) material, the nucleation rate is found to be enhanced,¹³⁻¹⁶ whereas the growth kinetics is reported to be unaffected at 1050 °C.¹⁵ The high density can be explained by several approaches like an enhancement of the density of nucleation sites in p+ material due to the presence of, e.g., B₂O₃ complexes.^{14,17} Alternatively, the O diffusivity in p+ material might even be further enhanced in the low temperature nucleation regime.¹⁸⁻²⁰ In addition, the surface energy and the misfit strain from the precipitates may be different in the presence of B.

In this paper, we compare nucleation rates in p+ and p- at 450 °C and the long time precipitation behavior at 900 °C in order to get quantitative access to the strain per precipitate, the surface energy and the nucleation rate. Further, these findings will be discussed in relation with existing models of diffusion-limited precipitate growth and B enhanced O dimer migration.

II. EXPERIMENTAL METHODS

A. Pendellösung oscillations

As described in detail in Refs. 6, 21, and 22, wedge shaped samples have been used to measure the average Bragg intensity as a function of the sample thickness and annealing time. This allows recording *in-situ* the increasing total strain which reflects directly the process of precipitate growth in the samples. The agglomeration process disturbs through strain the otherwise strictly periodic lattice potential and causes a shrinking average lattice phase. The lattice distortion becomes manifest in both an elongation of the Pendellösung length and an increase of the average Bragg intensity as function of sample thickness and annealing time. The former can be understood as the Eigenstates generating the Pendellösung oscillations rely on the characteristic of the periodicity of the lattice potential. The latter originates from an enlarged angular acceptance for the incident spherical

^{a)}will@krist.uni-erlangen.de

wave generating diffuse intensity proportional to the sample thickness. These two effects are correlated within the statistical dynamical theory^{23–26} through the static Debye-Waller factor E , which can be determined in our measurements with an accuracy of 10^{-4} . Furthermore, the initial slope of the increase of the Bragg signal and the timescale of the process give access to the misfit strain per precipitate, the diffusion constant, and the precipitate density.

B. Transmission electron microscopy (TEM)

TEM provides a complementary real space access to the density and the morphology of O precipitates. For TEM investigations 3 mm disks perpendicular to a $\langle 110 \rangle$ direction were prepared mechanically out of specimens I and II (see Table I) after the X-ray measurements including annealing procedures. These disks were subsequently thinned with a dimpler and final polished with 2 kV Ag⁺ ions under 4°–5° incidence angle using a Precision Ion Polishing System (PIPS, Gatan). The TEM investigations were carried out with a Philips CM30 microscope operated at 300 kV. The density of the precipitates was determined by counting the number of precipitates in bright field (BF) or dark field (DF) images taken under two beam conditions for (220) and (400). The foil thickness in the imaged sample areas was determined by convergent beam electron diffraction (CBED) and comparison with simulated CBED patterns obtained with the simulation program MBFIT written by Tsuda (<http://www.tagen.tohoku.ac.jp/labo/terauchi/personal/tsuda/tsuda.html>). The accuracy of the thickness measurement is estimated to 5 nm. The size and morphology of the precipitates were evaluated by BF imaging at higher magnification.

Specimen III was already used in a previous study,⁶ where the details of the TEM analysis are described.

C. Samples

Four Si wedges were prepared for the Pendellösung measurements according to the procedure described in Ref. 6. The B dopant concentrations and the thermal budgets are shown in Table I. The B concentration of sample I exceeds the O concentration by more than one order of magnitude and it is approximately three orders of magnitude higher than for samples II and III. The nucleation and precipitation behavior of this p⁺ wedge is compared to the behavior in p⁻ material with the same thermal budget (II) and a similar precipitate density (III). A long nucleation step of 141 h at 650 °C was set from which a precipitate density of $\sim 5 \times 10^{12} \text{ 1/cm}^3$ is expected according to literature,²⁷ and as confirmed later in this study. Specimen III was already used in a previous experiment.⁶ The growth temperature at 900 °C

was chosen for two reasons. First, the O diffusion constant D is well known to be $1.7 \times 10^{-12} \text{ cm}^2/\text{s}$ (Ref. 8) in this regime of normal (monomer) diffusion. Second, the diffusion is fast enough to monitor the kinetics within a reasonable timescale for the expected precipitate densities. Sample IV was cut from a float-zone material. This sample served as reference material to normalize the other measurements for thermal influences.

An X-ray diffractogram of the Pendellösung fringes of the 400 reflection was taken every 30 min with an exposure time of 10 min. The diffraction energy was 59.3 keV corresponding to the characteristic $K_{\alpha,1}$ -line energy of the tungsten x-ray tube at. The procedure is described in greater detail in Ref. 6.

III. RESULTS

A. Description within the statistical dynamical theory

To take the thermal influences into account, the Pendellösung length of the 400 Bragg peak was measured at 900 °C with a float-zone wedge (IV) to be $184.2 \mu\text{m}$. After background subtraction, the thickness dependent diffraction curves were described within the formalism of the statistical dynamical theory as demonstrated in Ref. 22. As an example, diffraction data of specimen I is shown in Figure 1 together with model curves according to the theory for several annealing times.

B. Kinetic curves for the static Debye-Waller factor

The extracted kinetic curves of $(1-E)$ are displayed in Figure 2, where $(1-E)$ can be considered as an overall measure for the imperfection, i.e., the integral strain in the crystal. In the model of statistically distributed spherical precipitates $(1-E)$ depends on the density of the precipitates ρ , the radius of the precipitates R and the misfit strain ϵ , as developed by²⁸ and described in more detail in Ref. 29. The evolution of $(1-E)$ in Fig. 2 displays several features. While the p⁺ sample shows the highest strain, its initial slope is comparable to specimen III but larger than for wedge II. The signal of wedge I reaches saturation after a characteristic time τ . This is comparable to the case of wedge III, but significant longer for wedge II. The amplitudes of the signal for sample I continue to rise even at the end of the experiment at 100 h and similar holds for sample II at the end of the annealing after 19.5 h. However, wedge II shows a saturation value of the signal after 35 h. These finding will be discussed in

FIG. 1. Experimental Pendellösung oscillations of the 400 reflection for wedge I at 900 °C and corresponding model curves from statistical dynamical theory after annealing times of 0, 2.5 h, 5 h, 7.5 h, and 10 h (light grey to black).

TABLE I. Dopant concentrations and thermal budgets of wedges.

Sample	[B] [$1/\text{cm}^3$]	[O _i] [$1/\text{cm}^3$]	Temperature profile
I	4×10^{18}	5.8×10^{17}	10 h 450 °C + 100 h 900 °C
II	3×10^{15}	8×10^{17}	10 h 450 °C + 100 h 900 °C
III	1.6×10^{15}	6×10^{17}	141 h 650 °C + 19.5 h 900 °C
IV	$< 10^{13}$	$< 10^{15}$	900 °C

FIG. 2. (1-E) kinetic curves for the three specimens (diamonds sample I, crosses sample III, squares sample II) as a function of the annealing time at 900 °C.

Sec. IV in terms of a diffusion-driven growth process followed by a second growth regime.

IV. ANALYSIS OF DIFFRACTION DATA IN TERMS OF OXYGEN PRECIPITATION

A. Description within Ham's theory of diffusion-driven growth

Within the theory of a diffusion-driven growth process, the radius of the SiO_x precipitates increases for short times or equivalent to a high O supersaturation proportional to the square root of the time $t^{1/2}$. When a significant amount of O is consumed, the supersaturation has become reduced and the growth approaches an exponentially damped behavior before going into saturation. This is described by Eq. (1)^{7,30}

$$t/\tau = \int_0^x \frac{x(t)dx}{1-x(t)^3} \quad \text{with } x(t) = R(t)/R_{\max}, \quad (1)$$

where τ is the characteristic timescale for the process represented by Eq. (2). $R_{\max}$ is the maximum possible radius (see Eq. (3)) determined by the initial supersaturation S_0 (see Eq. (4)) of O in Si

$$\tau = (3/(4\pi))^{2/3} D^{-1} S_0^{-1/3} \rho^{-2/3}, \quad (2)$$

$$R_{\max} = \left(\frac{3S_0}{4\pi\rho} \right)^{1/3}, \quad (3)$$

$$S_0 = \frac{[O_i]_0 - [O_i]_{\text{eq}}}{[O_i]_{\text{prec}} - [O_i]_{\text{eq}}}. \quad (4)$$

In Eq. (4) $[O_i]_0$, $[O_i]_{\text{eq}}$, and $[O_i]_{\text{prec}}$ are the initial interstitial O concentration (see Table I), the equilibrium solubility at 900 °C (2.65×10^{16} atoms/cm³ (Ref. 1)), and the O concentration in the precipitated phase (2.9×10^{22} atoms/cm³ (Ref. 31)), respectively. Since in Eq. (2), all values with exception of the

FIG. 3. Dependence of typical timescale parameter τ on the density of the precipitates ρ for an initial O concentration of 6×10^{17} atoms/cm³ and 900 °C.

precipitate density are known, one can readily obtain a starting value for ρ from the data. This is demonstrated in Figure 3 for an initial O concentration of 6×10^{17} atoms/cm³.

The initial linear signals extend to 3.5 h, 9 h, and 2 h for specimens I, II, and III, respectively. With the O concentrations given in Table I, the precipitate densities can be calculated and they are listed in Table II. These densities do not influence the further data treatment. However, the extracted densities from the formalism of a diffusion-driven growth process should be very close to these approximated values. This demonstrates the high sensitivity of the present technique to ρ under the assumption that the diffusion constant is known.

The kinetic curves yield additionally information about ρ , D , and ϵ through the initial slope m of the signal. Thus, from the three determined parameters (E , τ , m), the three unknown variables (R , ρ , ϵ) can be determined.

The first step for a quantitative data analysis is to calculate R as a function of time from E (for details, see Ref. 6). Unfortunately, ρ and ϵ are required to do so which are at this point unknown. However as shown above, they are available through the kinetic curve. This difficulty can be overcome through a recursive data treatment and it has been realized through the following procedure. First, values for ρ and ϵ are chosen arbitrarily. In a next step, $R(t)$ is calculated with these values through Eqs. (3) and (4) in Ref. 6, and $R(t)$ is fitted through Eq. (1). This yields the diffusion constant D and a new value for ρ , which is used to calculate $R(t)$ again via Eqs. (3) and (4) in Ref. 6 with the same ϵ and subsequently fitted with Eq. (1). This procedure is repeated until the density adopts a stable value. This recursive procedure is repeated for various ϵ values. The set of ϵ , ρ , and $R(t)$ for which found diffusion constant at the end of the recursion

TABLE II. Precipitate densities for the different samples from the time-scales τ of the initial linear signal increase.

Specimen	τ [h]	$[O_i]$ [1/cm ³]	$\sim\rho$ [1/cm ³]
I	3.5	5.8×10^{17}	3×10^{12}
II	9	8×10^{17}	6.5×10^{11}
III	2	6×10^{17}	7×10^{12}

FIG. 4. Evolution of R as a function of annealing time at 900 °C for specimen II. The grey curve representing a diffusion-driven growth process describes the data well over the whole range of data points.

procedure matches the literature value ($1.7 \times 10^{-12} \text{ cm}^2/\text{s}$) is used.

This procedure works well within the whole data range for specimen II as illustrated in Figure 4. However, this is not the case for samples I and III. Nevertheless, this procedure is still applicable in a certain time range, i.e., from 0 to 8.5 h (I) and from 0 to 4 h (III). The description within the diffusion-driven growth process (Eq. (1)) is shown in Figures 5 and 6 by the grey curve fitted in the time range given above, but graphed for the entire time range measured. It is not possible to find a set of parameters (ρ , ϵ), which reproduces the data over the entire annealing process by a diffusion-driven growth process only. At this point, it should be mentioned that a purely diffusion-driven growth process according to Eq. (1) would show a saturation value of the average particle size, as the grey lines indicate (I and III) and as specimen II shows for the long time annealing behavior. We attribute the observed discrepancy (Figs. 5 and 6) to a second growth regime, which becomes relevant at longer annealing times. An explanation and interpretation of the second growth regime is given in Sec. IV B, whereas for the moment, the analysis focuses on the first growth regime. The results from the recursive fitting procedure are summarized in Table III. First, the initial precipitate densities derived from the typical timescales of the process (Table II) are very close to the ρ values from an analysis within the whole

FIG. 5. Evolution of R as a function of annealing time at 900 °C for specimen I. The grey line is a fit curve for a diffusion-driven growth process (Eq. (1)) for the data from 0 to 8.5 h. The black curve is a fit of the remaining data points with a $t^{1/3}$ law expected for Ostwald ripening.

FIG. 6. Evolution of R as a function of annealing time at 900 °C for specimen III. The grey line is a fit curve for a diffusion-driven growth process (Eq. (1)) for the data points from 0 to 4 h. The black curve is a fit of the remaining data points with a $t^{1/3}$ law expected for Ostwald ripening.

formalism. Second, ϵ is highest in sample I, implying the strain per precipitate to be higher in the highly doped material independent of the thermal budget or the precipitate density ρ . Third, the density in the highly doped material is for the same thermal budget about seven times increased as compared to the moderately doped material, even the moderately doped material had a higher initial O content.

B. Ostwald ripening as long term behavior

Two problems for describing the entire range of data are left. On the one side, a model for the long time precipitation behavior, on the other side the question, why the second growth regime does not affect specimen II. Relating to the long time behavior, Ostwald ripening appears to dominate. This model is capable of describing the observed increment of the overall strain since the average radius of the precipitates continuous to grow introducing additional strain in exchange for a reduction of the total surface energy. Moreover, the effect of this process becomes reduced with time as observed. Further, Ostwald ripening has been observed for SiO_x precipitates in nitrogen doped Si.³² The theory of coarsening in a two component system under the condition of mass transport was developed by Wagner.^{33,34} It describes the ripening of spheres due to solubility changes at the precipitate lattice interface in only slightly supersaturated solutions as a function of the precipitate surface curvature. It does not take into account the strain caused by the precipitates, which is expected to slow down the coarsening. Within this theory, the average particle radius grows according to Eq. (5)

$$\langle R \rangle = (4/9 \text{ Kt})^{1/3}. \tag{5}$$

TABLE III. Fit results for the initial diffusion-driven growth regime including the range of observed radii (calculated out of (1-E)).

Sample	ϵ	ρ [$1/\text{cm}^3$]	R [nm]
I	0.294	5.5×10^{12}	3.9–10.8
II	0.098	7.9×10^{11}	9.8–20.3
III	0.215	9.1×10^{12}	3.8–8.8

The growth constant K represents the average ripening rate of the precipitate volume per time unit. In the simplest approach of an ideal solution, it can be written as

$$K = \frac{2V_{\text{prec}}^m \sigma D([O_i]_{\text{eq}}/[Si])}{([O_i]_{\text{prec}}/[O_i + Si]_{\text{prec}})^2 R^{\text{id}} T}, \quad (6)$$

V_{prec}^m is the molecular volume in the precipitate, which can be calculated with $[O_i]_{\text{prec}}$ to $1.12 \times 10^{25} \text{ Å}^3/\text{mol}$ under the assumption that the chemical composition of the SiO_x precipitates is $\text{SiO}_{1.17}$.³¹ The surface energy of the precipitates σ drives the ripening process. $[Si]$ and $[O_i + Si]_{\text{prec}}$ are the densities of Si atoms in the Si lattice and of O plus Si atoms in the precipitated phase, respectively. R^{id} represents the ideal gas constant and T the temperature. The surface energy σ as the only unknown parameter can be determined within the assumptions described above. The data for specimens I and III clearly show that the coarsening during the second growth regime leads to a comparable signal enhancement. This indicates that the surface energies of the precipitates in the two specimens are of similar value. To quantify this and to compare the extracted σ to literature, the data was fitted with Eq. (7)

$$\langle R \rangle = R_0 + (A(t - t_0))^{1/3}. \quad (7)$$

The fit and the calculated σ values are summarized in Table IV, and the fit curves are displayed as black curves in Figures 5 and 6. The extracted values for σ are (i) close to each other as expected from the amplitudes of the second growth regime and they are (ii) close to literature values of 100 to 800 erg/cm²,^{35–38} even when they are lower by a factor of five to six. This might have several reasons. The most obvious is that the theory of Ostwald ripening after Wagner is derived for a very specific case of strain free spherical precipitates. In the case of O in Si, the precipitates obviously generate a size dependent strain and the precipitates must not have a spherical shape. Additionally, the initial size distribution and the density of precipitates might influence the coarsening behavior. Unfortunately to our knowledge, no model exists for such complicated systems. This point together with arguments why coarsening is retarded in sample II will be discussed chapter V. For the moment we state, that strong implications exist that Ostwald ripening can occur with comparable amplitude in highly and in moderately doped material. The amplitude of the ripening yields σ values in the right order of magnitude, compared to literature.

TABLE IV. Values of the volume ripening rate per hour A and of the surface energy per area σ . No second growth regime was observed for sample II.

Sample	$A [\text{Å}^3/\text{h}]$	$\sigma [\text{erg}/\text{cm}^2]$
I	73 ± 30	64 ± 26
II	./:	./:
III	80 ± 40	70 ± 35

TABLE V. Comparison of the density ρ and precipitate volume V after the annealing from diffraction data labeled as diff with TEM data labeled TEM . Further listed are the aspect ratio γ from TEM and the misfit strain ϵ from diffraction.

Sample	$\rho_{\text{diff}} [10^{12}/\text{cm}^3]$	$\rho_{\text{TEM}} [10^{12}/\text{cm}^3]$	$V_{\text{diff}} [\text{nm}^3]$	$V_{\text{TEM}} [\text{nm}^3]$	γ_{TEM}	ϵ_{diff}
I	5.5	2.8	4988	5316	1:4.4	0.294
II	0.79	0.91	35 041	40 678	1:15.6	0.098
III	9.1	10	2840	3072	1:10.6	0.215

C. TEM investigations

The specimens were characterized with TEM after the X-ray measurements including the annealing procedure. The results for specimen III have already been presented in a previous publication.⁶ For this specimen, a comparison of the X-ray and TEM data shows that the densities are remarkably close to each other. Additionally, the volume per precipitate differs only within 8% (see Table V). The morphology of the precipitates was determined to be plate-like with an average dimension of (32 nm $\times$ 32 nm $\times$ 3 nm).

As described above, specimens I and II were prepared for TEM investigation in $\langle 110 \rangle$ -projection. A typical DF image acquired in a (400) two beam case is shown in Figure 7. In order to determine the volume density ρ of the precipitates, the local thickness of the TEM foil has to be known. For this, a CBED pattern has been taken in the center of the imaged sample area using the same two-beam condition for (400) (Figure 7, bottom). The fringe contrast in the bright-field and dark-field CBED disks correspond to dynamical rocking curves (thickness fixed, excitation error varies) and are well described by the two-beam dynamical theory of electron diffraction as demonstrated by the good correspondence with the simulated CBED pattern. The rocking curve fringe pattern is a unique function of the sample thickness and the extinction (or Pendellösung) distance ξ_g of the reflection $g = (400)$ and can in principle be used to determine both parameters (Williams & Carter). However, since the extinction distance in Si is well known for 300 kV electrons ($\xi_g = 187 \text{ nm}$), it is kept fixed in the simulation and the sample thickness is determined by comparison of the

FIG. 7. 220 reflection dark field (left) and CBED pattern (right) of the 000 reflection and the 220 reflection of a representative sample volume of specimen II. To determine the foil thickness and thus the precipitate density ρ , the experimental CBED pattern (up) is compared with a simulation (down). For the simulation, a sample thickness of 380 nm and an acceleration voltage of 300 kV are used.

FIG. 8. 004-(left) and 220-(right) DF-(top) and BF-images (bottom) of the identical platelet lying edge-on in a $\{001\}$ plane found in sample II.

experimental CBED pattern with simulated CBED patterns obtained for different sample thickness values. In order to evaluate the shape of individual precipitates, it is important to compare images taken under different two beam conditions, as illustrated in Figure 8. The BF and DF images taken under two beam condition for (004) show pronounced strain contrast making it difficult to unambiguously determine the shape of the precipitate. In contrast, the images taken under two beam condition for (2–20) clearly reveal that the precipitate has a plate-like character and lies on the (001) plane. From the smallest width of the contrast, the thickness of the precipitates can be roughly estimated. This is not possible for platelets lying on inclined (100)- or (010)-planes.

For specimen I, 30 precipitates were counted in several images leading to a density of $2.8 \pm 0.5 \times 10^{12} \text{ 1/cm}^3$, which is lower by a factor of two as compared to the above results from the X-ray diffraction. The morphology was found to be plate-like with an average edge length L of 28.6 nm and an average thickness of 6.5 nm. The former was determined from eight, the latter from three (edge-on) precipitates. The average volume is remarkably close within 7% to the results from the Pendellösung measurements. The aspect ratio y is approximately a factor of 2.5 higher than for the precipitates in specimen III, although it should be mentioned that measuring y via strain contrast is not as precise as the EDX (Energy-Dispersive X-ray spectroscopy) data acquired for sample III.⁶ However, it is possible to take the conservation of the O amount into account since at the end of the annealing procedure nearly the whole O is located in the precipitates. Under the assumption that the O concentration in the Si lattice has fallen down to its solubility limit $[O_i]_{\text{eq}}$, the thickness of the platelet t is given through Eq. (8)

$$t = \frac{[O_i] - [O_i]_{\text{eq}}}{\rho [O_i]_{\text{prec}} L^2}. \quad (8)$$

Equation (8) yields a thickness of $\sim 8.3 \text{ nm}$ using the TEM density and $t \sim 4.2 \text{ nm}$ with the density extracted from the Pendellösung measurement. From this y should be in the range of 1:3.4 to 1:6.7. These findings support the extracted platelet thickness and aspect ratio y as provided by the TEM images from edge-on precipitates and denoted in Table V.

The TEM images of specimen II lead to a density of $9.1 \pm 1.2 \times 10^{11} \text{ 1/cm}^3$ by counting 58 precipitates. This is identical within the error bars to the value from the diffraction experiments. Again plate-like precipitates lying in $\{100\}$ planes are observed. Average edge length and thickness were 86 nm and $\sim 5.5 \text{ nm}$, respectively. The former was determined from eight, the latter from three precipitates. The resulting aspect ratio is 1:15.6, which is 20%–30% lower than the range 1:19 to 1:21.5 determined through Eq. (8). Representative sample volumes and TEM images are shown in Figures 7 and 8. The average volume per precipitate is again close within 15% to results from Pendellösung measurements.

In conclusion, the agreement for the parameters ρ and V for the samples I, II, and III as extracted from TEM and dynamical X-ray diffraction is convincing. The biggest deviation by a factor of nearly two is found for the density ρ in the p+ Material. This might originate from the relatively small and maybe not representative sample volume investigated by TEM. Additionally, it is possible, that the diffusion constant, which was fixed to the literature value during the diffraction data evaluation, might be somewhat influenced in the p+ material at 900 °C. However, such a deviation is not reported in literature. Also, the present data shows that such a deviation cannot be higher than ~ 1.5 (Eq. (1)–(4)). Another maybe surprising result is that the aspect ratio does not influence the densities and dimensions found in the diffraction experiment. In fact the aspect ratio y seems to influence the strain ϵ , which appears to depend on the morphological shape as expressed by y .

V. DISCUSSION

A comparison of ρ in the p+ and p- material after an identical nucleation step at 450 °C for 10 hours shows a ~ 7 times higher density in the p+ material. According to nucleation theory, the nucleation rate J depends on D , $[O_i]$, ϵ , σ , S_0 and the nucleation site density N_0 . In the low temperature regime, where the O dimer is supposed to control the O transport,²⁰ J is described by Eq. (9)

$$J \sim [O_i]^2 D_{O_2}(\epsilon_f) f(\sigma, \epsilon, S_0) N_0. \quad (9)$$

Here, $f(\sigma, \epsilon, S_0)$ is a function of the surface energy, the misfit strain, and the degree of supersaturation as described, e.g., in Ref. 38. $D_{O_2}(\epsilon_f)$ is the O dimer diffusion constant, which depends on the type of dopant (e.g., arsenic, boron, phosphorus) and on the dopant concentration. The biggest impact might have the Fermi level ϵ_f ,²⁰ which changes with both the type of dopant and the concentration. According to Ref. 20, the diffusion constant in highly B doped material is enhanced in the temperature range from 400 to 550 °C by a factor of ~ 8 to 25, but a function of the dopant concentration. In this study, the B concentration was $3 \times 10^{18} \text{ 1/cm}^3$ and thus close

to specimen I. By taking into account the difference of the square (Eq. (9)) of the O concentration between I and II, the enhanced nucleation rate corresponds to an enhanced diffusion of ~ 13 . Thus, it can be explained by B enhanced dimer diffusion without a need of other mechanism like a heterogeneous nucleation at B_2O_3 sites or a lower surface energy in p+ material due to B incorporation. On the other hand, the overall strain in the p+ material is much higher than in the p- material. This may be due to a higher volume misfit, but it may also be correlated with the morphology of the precipitates. The results presented in Table V suggest that ϵ and y are coupled parameters in the sense that a lower ϵ value is expected with an increasing value of the aspect ratio y . Another indication that σ cannot explain the discrepancy in the nucleation kinetics is provided by the analysis of the second growth regime, which yields comparable σ values for p- and p+ materials.

The question remains, why the second growth regime was not observed in specimen II. First, it is obvious that the shape and the strain of the precipitates influence the coarsening behavior. With shrinking y the curvature and thus the driving force shrinks. In addition, the strain increases with the size of the precipitates, which retards the coarsening behavior. As denoted in Table V, specimen II shows the biggest precipitates with the highest aspect ratio, which in combination retards the ripening.

Second, the mobility of the O has to be considered, since during coarsening O has to migrate between the precipitates. The diffusion length is given by Eq. (10)

$$L = \sqrt{Dt}. \quad (10)$$

The average free path between two precipitates $(1/\rho)^{1/3}$ is $0.56 \mu\text{m}$ and $0.46 \mu\text{m}$ for samples I and III, respectively, whereas it calculates to $1.08 \mu\text{m}$ for sample II. An O atom needing less than half an hour to diffuse from one precipitate to the next samples I and III, needs ~ 2 h for sample II. Thus, for low precipitate density and low mobility, the coarsening will also be retarded. However, a 2 h timescale should still be well observable within the duration of our experiment, and the coarsening effect should rather be delayed than missing. Hence for the present, we are not able to explain this fully. But the three reasons for retardation are given, which in combination might slow the Ostwald ripening in sample II down to a level, which becomes unobservable in the experiments described.

VI. CONCLUSION

Pendellösung measurements have been conducted on three Czochralski wedges with different B dopant concentrations during annealing at 900°C . A recursive fitting procedure allows to determine the density ρ of precipitates, their mean radius as a function of annealing time $R(t)$, and the misfit strain ϵ from a combination of the in-situ measured static Debye-Waller factors and their evolution with time. The results are interpreted within the model of a diffusion-driven growth process. A comparison with TEM measurements shows that the diffraction based technique is sensitive

to ρ and the dimension of the precipitates, whereas the explicit morphology is not directly provided. In addition, monitoring the kinetic curve shows two different growth regimes. The long time growth regime is interpreted as Ostwald ripening, and a comparison between samples I (p+) and III (p-) shows σ values close to each other and also in agreement with literature values. ϵ is found to be highest in the p+ material regardless if the p-material has a comparable density or the same thermal budget. For all three samples, the TEM measurements show plate-like precipitates whose aspect ratio ranges from 1:4.4 (I) over 1:10.6 (II) to 1:15.6 (III) and thus is the lowest for the p+ specimen, which has the highest misfit strain value. Thus, from these findings ϵ seems to be connected to y and provides indirect information about the morphology of the precipitates. This is not too surprising since the integral strain energy also scales with y .³⁹ ρ was found to be a factor of ~ 7 higher in I compared to the p-specimen with the same thermal budget (II). This difference in ρ can be explained with B enhanced O dimer diffusion without the need of boron oxygen complexes as nucleation centers and is thus an indirect proof of the diffusivity measurements by Zeng *et al.*²⁰

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