

Study on defect annealing potential and bulk micro defect formation using high temperature RTA conditions for Cz-grown silicon

Timo Müller^{*1}, Michael Gehmlich¹, Gudrun Kissinger², Dawid Kot², Andreas Sattler¹, Alfred Miller¹, and Erich Daub¹

¹ Siltronic AG, Hanns-Seidel-Platz 4, 81737 München, Germany

² IHP, Im Technologiepark 25, 15236 Frankfurt (Oder), Germany

Received 8 March 2017, accepted 20 May 2017

Published online 27 June 2017

Keywords CZ silicon, oxide precipitation, rapid thermal annealing, vacancy

* Corresponding author: e-mail timo.mueller@siltronic.com, Phone: +49 8677 836884, Fax: +49 8677 886 9736

In this paper, the key parameters of a rapid thermal annealing (RTA) nitriding step are discussed with respect to vacancy- and oxygen precipitate (BMD)-profile formation. These RTA key performance parameters are the maximum NH₃ dissociation temperature (i), the temperature stability of the stored vacancy peak (ii), and the defect dissolution capability of self Si agglomerates at elevated temperatures (iii). This parameter study could be helpful for a future model of the vacancy in-diffusion

process into the Si near surface region. Especially the gate oxide integrity (GOI) is an important parameter to establish long life cycles in current memory devices. After NH₃ RTA processing, it was surprisingly found that the GOI defect level is still influenced by small-sized grown in particles. It is demonstrated that a complete restoration toward a high GOI signal can be achieved via a 1300 °C RTA step. The gate oxide integrity is afterwards as good as observed on a defect free polished CZ wafer.

© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction One of the key-techniques in state of the art microelectronic engineering to process high performance devices like DRAM, 2D/3D NAND is the near surface defect control on the nanometer scale. Typically, the defect behavior in CZ silicon is controlled by e.g., magnetic fields for oxygen control and tight v/G control to ensure the absence of larger grown-in defects originating from either interstitial or vacancy supersaturation [1]. The term “ v/G ” control (v = crystal pulling speed, G = thermal gradient at the melt/crystal interface) was at first described by Voronkov [19] to distinguish the fundamental different crystal pulling regimes in which Si-vacancy agglomerates (= “voids”), respectively, Si-interstitial agglomerates occur in the Si-crystal.

In addition, an internal gettering is needed to assure the absence of metal atoms in the active device layer. This internal getter is typically formed by oxygen precipitates (also called bulk micro defects (BMDs)). They need to be formed in a typical density ($>1\text{E}9/\text{cm}^3$) and depth ($>$ a few

μm) to ensure both sufficient gettering and stable device performance.

Rapid thermal annealing (RTA) is an appropriate method for defect engineering. RTA can dissolve small defects like voids or small-sized precipitates and store vacancies in a specific depth from the surface. This is achieved via elevated temperatures $\sim 1300^\circ\text{C}$ and, respectively, via NH₃ dissociation at the surface at temperatures $>1150^\circ\text{C}$ [2–4].

In this work, the key parameters of defect dissolution and BMD formation at ultrahigh temperatures $\sim 1300^\circ\text{C}$ are discussed. A nitriding step to generate vacancy and BMD-profiles is reviewed with respect to needed maximum NH₃ dissociation temperature and temperature stability of the stored vacancy peak which itself is monitored via Pt diffusion.

Especially the gate oxide integrity (GOI) is an important parameter to establish long life cycles in current memory devices. After NH₃ RTA processing it was surprisingly

found that the GOI is still influenced by small grown-in particles. It is demonstrated that a complete restoration toward a high GOI can be achieved via a 1300 °C RTA step. The gate oxide integrity is afterwards as good as observed on a defect free polished CZ wafer. This effect is different from GOI deterioration found after RTA processing of wafers from fast-pulled v-rich crystals [5].

2 Experimental The samples used in this study were p-type (boron-doped, 7–14 Ohm cm), mirror polished, (001) oriented 300 mm Czochralski (CZ), and magnetically pulled Czochralski – Si wafers [1, 16, 17]. MCZ is used to control and reduce the Oi content of the Si wafer by partly freezing the melt in contrast to standard CZ pulling approaches. The oxygen and nitrogen concentrations for the CZ group were 6-7E17/cm³ and 1-3E14/cm³, respectively. The oxygen concentration for the MCZ group was 5-6E17/cm³ (both new ASTM). The initial sizes of the void defects in the CZ wafer were measured by infrared laser scattering tomography (IRLST). The average and maximum sizes were approximately 40 and 80 nm, respectively. The MCZ wafers were nearly defect-free in regard of the IRLST measurement.

The RTA was conducted with holding times of 10–150 s at each temperature in the range from 1100 to 1310 °C. The gases were pure O₂, Ar, or Ar/NH₃ mixed gases. RTA heating rates were typically between 25 and 80 K s⁻¹, the cool down rates were typically 35 K s⁻¹.

After the RTA treatment, the wafers were chemical-mechanical polished (CMP) removing >15 µm for the GOI tests and >=1 µm for the BMD tests. Existing oxynitride films were removed before CMP by an HF containing wet clean. The BMDs were grown after the RTA treatment by applying a thermal cycle of 3 h at 780 °C and 16 h at 1000 °C in 100% O₂, in the following called two step anneal. The BMD density and the depth of the defect denuded zone were measured by IRLST. The gate oxide integrity test consists at first of a dry oxidation process of 25 nm thickness. Secondly a poly-Si gate was deposited and annealed to reduce the contact resistance between Poly-Si and the gate oxide. The gate surface was patterned in typically 0.6 cm² gate areas by wet chemical etching being quite similar to that method in Ref. [2]. Most of the observed oxide failures occur at critical electrical fields called “B-mode” of 4–8 MV cm⁻¹.

Vacancy profiles were measured on wafers after NH₃ – RTA by Pt in-diffusion [6, 11, 12, 15] at 730 °C for 1 h. The highly mobile interstitial Pt atoms occupy lattice vacancies thus forming substitutional Pt (Pt_s) according to the Frank–Turnbull mechanism [14]. Substitutional Pt can easily be detected by deep level transient spectroscopy (DLTS) in both p-type and n-type Si [14]. In p-type material, two levels related to Pt_s at E_V + 0.067 eV and E_V + 0.330 eV exist. Although both can be used to determine the Pt_s concentration, we preferred the level at E_V + 0.330 eV because of the higher peak temperature. The vacancy concentration C_V can be obtained from the following relationship [11, 12]:

$$C_V = C_{Pt} \left(1 + \frac{C_V^{eq}}{C_{Pt}^{eq}} \right) \quad (1)$$

where C_{Pt} is the Pt_s concentration measured and C_V^{eq} and C_{Pt}^{eq} are the equilibrium concentrations of vacancies and Pt_s at the wafer surface, respectively. The latter two can be found in Ref. [11].

3 Results and discussion

3.1 Defect dissolution in void rich RTA –

O₂-treated samples At first the defect dissolution by an RTA step partly similar as described in Ref. [5] – but at elongated holding times – was analyzed. The void density was measured by IRLST and found to be nearly zero (Fig. 1a) compared to the non-RTA-treated Si wafer exhibiting void defect densities of 1–4E7/cm³ (Fig. 1b). The void dissolution was only effective in oxygen ambient as the interstitial injection from the growing oxide supports the void annihilation [5].

3.2 BMD formation in void rich RTA – O₂-treated samples At longer holding times than given by Ref. [5] of ~30 s, the BMD density disappears in the bulk when a “two

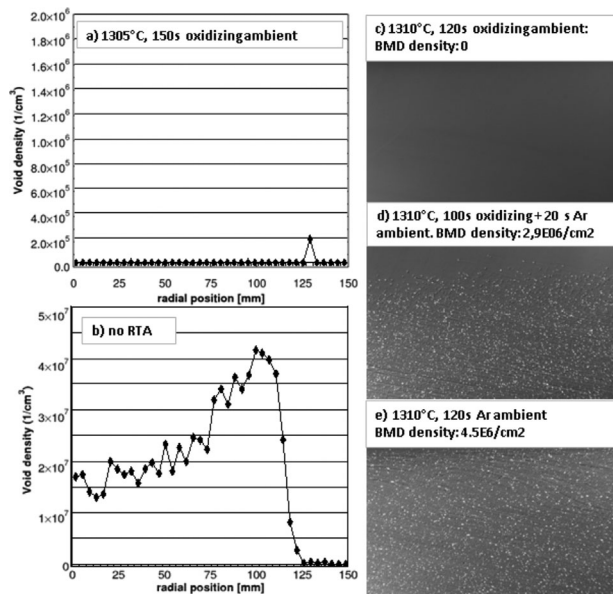


Figure 1 Processing at 1305 °C, holding time of 150 s in O₂: complete void dissolution (a) of fast-pulled CZ-Si wafer containing nitrogen and oxygen was found. The virgin wafer exhibited a radial inhomogeneous void profile (b). Processing at 1310 °C, holding times of 120 s versus 100 s in O₂. Surprisingly no BMD formation was found after the two step anneal if a critical holding time of 120 s was reached (c). In contrast BMD formation similar to Refs. [5, 7, 8] was observed at still shorter holding times (d) in combination with a 20 s Argon post step or in pure Argon ambient (e). The BMD density was measured via Secco etching of ~1 µm removal and followed by optical microscopy.

step anneal” is applied as can be seen in Fig. 1c (here the BMD density was always zero if a holding step at 1200 °C of 15 s was applied during cool down. Otherwise the BMD density was low at $\sim 3 \times 10^5/\text{cm}^2$). The effect of vacancy generation in the wafer bulk starting at $T > 1300^\circ\text{C}$ and prominent at $T = 1350^\circ\text{C}$ as discussed in Ref. [5] can be characterized in terms of the key parameter $C_v - C_i$. (C_v is the concentration of vacancies and C_i is the concentration of interstitials.) This term is the difference of vacancy and interstitial concentration after RTO (RTA processing in 100% O_2). If this difference is $> 9\text{E}12/\text{cm}^3$ the oxygen precipitation starts mainly in the bulk. While we still found precipitation at 1310 °C for a holding time of 100 s (Fig. 1d), it disappeared for holding times of 120 s (Fig. 1c). One has to take into account that the RTA process has not been finished after 100 s in case of Fig. 1d but consists of a 20 s longer holding time while the ambient is diluted from 100% O_2 to an Ar/O_2 mixed ambient. The vacancy concentration can therefore somehow also be influenced/increased by this stop of further oxidation and partly changing to an Argon/ O_2 ambient. The usual strong precipitation in a non-interstitial injecting ambient like argon was observed too (Fig. 1e) at these longer holding times. The precipitation formation was therefore comparable as demonstrated in Ref. [5] but smaller denuded zones of $\sim < 20 \mu\text{m}$ are formed.

The inhibited precipitation behavior at holding times of 120 s in a pure RTO process (Fig. 1c) indicates that the mechanism of monotonous increase of $C_v - C_i$ at $T > 1300^\circ\text{C}$ might only be applicable until a certain holding time is reached. In this case, the parameter $C_v - C_i$ might be considered to be $< 9\text{E}12/\text{cm}^3$ and therefore too low for oxygen precipitation.

3.3 Vacancy profiles generated by nitriding RTA steps

One of the known RTA processes for BMD enhancement in the surface vicinity called proximity gettering is the use of a nitriding ambient like NH_3 [9]. The results of applying NH_3 ambient in an RTA step on MCZ Si wafers with rather low O_i concentration ($5.0\text{--}5.4\text{E}17/\text{cm}^3$) is shown in Fig. 2. As already stated in Ref. [9] a “proximity gettering” can be observed via formation of a BMD peak close to the surface. In Ref. [9], the BMD density at the peak was found to be $\sim 3\text{E}10/\text{cm}^3$ and the bulk density $\sim 2\text{E}9/\text{cm}^3$ for RTA temperatures of 1150 °C. In the case of MCZ wafers, the BMD densities are lower in the peak and bulk region and the temperature dependence is different. The critical temperature of 1150 °C can be seen as the onset of enhanced BMD formation still missing the characteristic BMD peak near the surface. This feature is only observed at higher temperatures like 1175 °C and might be attributed to the generally lower BMD formation capability of this defect optimized material with a very low concentration of interstitial oxygen. Similar experiments using nitride layers created preliminary at 1100 °C in NH_3 ambient by rapid annealing followed by a 1220 °C 10 s RTA step in Argon were demonstrated in Ref. [20]. In one example the nearly same thermal treatment

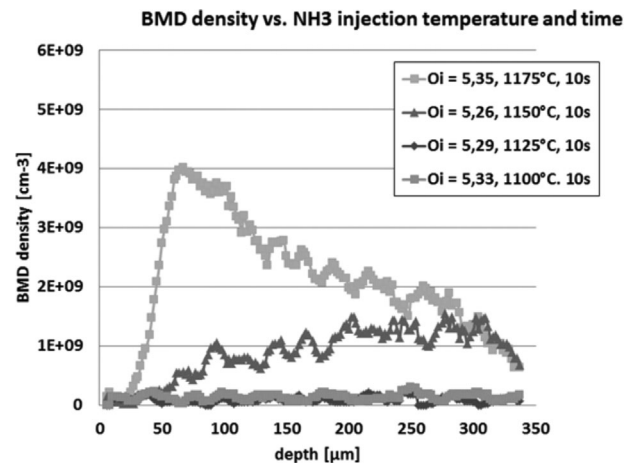


Figure 2 Vertical BMD formation after NH_3 RTA steps at different holding temperatures. At $T = 1150^\circ\text{C}$ the onset of enhanced BMD formation occurs.

post the RTA steps (800°C 4 h + 1000°C 16 h in O_2) were applied at similar substrates (P-wafers, oxygen concentration $\sim 5 \times 10^{17} \text{cm}^{-3}$) than presented in Fig. 2. The peak formation was also observed but at a distinctly smaller distance from the surface ($15\text{--}20 \mu\text{m}$) compared to the BMD peak position of the 1175°C 10 s RTA test ($\sim 60 \mu\text{m}$, Fig. 2). Also the reported BMD peak height was $\sim 8 \times 10^9/\text{cm}^3$ roughly a factor of two bigger. This difference in BMD peak density and position might be attributed to the two different approaches to create the nitride respectively oxynitride film. In the case of Ref. [20], the described two consecutive RTA steps are generating more effectively the BMD peak via vacancy injection building a much smaller denuded zone than in the one step NH_3 RTA process as shown in Fig. 2.

3.4 Stability and integrity of the vacancy profiles generated by nitriding RTA steps

Shin et al. [2] studied the impact of an NH_3 ambient on void-rich Si wafers and found gate oxide deterioration (GOI) depending on the v/G setting of the 300 mm crystal. Successive re-polishing steps via CMP led to a decrease of the GOI defect rate as a “nano-void” layer was removed. This defect layer was created by the vacancy generating NH_3 RTA step. Such an RTA step is generally leading to an inhomogeneous vacancy or VO_2 profile [4] during cool down.

The first question is now how stable is such a stored profile against further temperature cycles e.g., in a chip manufacturing process. Secondly: is the GOI deterioration effect found also in nearly defect free MCZ wafers?

3.4.1 Stability of vacancy profiles from NH_3 RTA steps

In order to test the stability of the stored vacancy profiles, a test cycle was applied in one case, before the RTA step and in another case after the RTA step (Fig. 3). A temperature of 1140°C was chosen because vacancies are still mobile but the well-known effect of vacancy

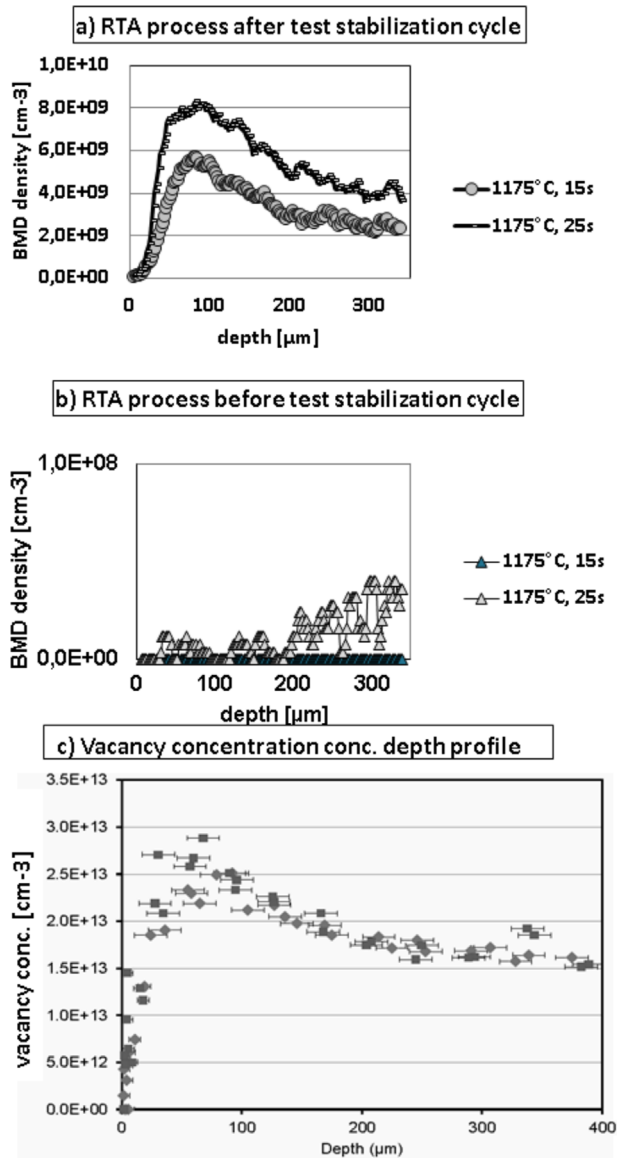


Figure 3 BMD density depth profiles if the NH₃ RTA step is located (a) *after* and (b) *before* a so called “test stabilization cycle.” The residual vacancy concentration measured by Pt depth diffusion (c) was only found after the process sequence (a): stabilization test cycle + NH₃ RTA step.

enhancement via high RTA temperatures >1200 °C [10] is not yet dominant. The stabilization test cycle consisted of a temperature profile as follows: ramp up with 20 K s⁻¹, hold at 1140 °C for 150 s and ramp down with 20 K s⁻¹. If this cycle is applied before the NH₃ RTA step, the BMD profiles after the two step anneal resembles that of a pure NH₃ RTA step at processing temperatures of ~1175 °C (Fig. 3a).

If the test cycle is applied after the NH₃ RTA step (Fig. 3b) then the BMD peak disappears and – depending on the NH₃ exposure time – is completely absent in the bulk for exposure times of ~15 s or below 5E7/cm³ if the exposure time is ~25 s.

The vacancy concentration versus the depth was measured by Pt diffusion post the process sequence of Fig. 3a. Its depth dependence is qualitatively similar to the BMD depth profile. It was not visible if the process sequence of Fig. 3b was applied. Vacancy profile measurements using this Pt diffusion technique were also applied in Ref. [21] at RTA processes in Argon ambient. The stability of the generated vacancy profiles were probed at two different temperatures (950 and 975 °C) and two different holding times (18 and 58 s) and showed a typical Arrhenius dependency. This approach would be also useful here to learn more about the specific type of vacancy generated during the NH₃ RTA process. Future experiments are therefore necessary at varying temperatures of the stabilization test (e.g., 1100 and 1120 °C).

3.4.2 GOI deterioration in NH₃ RTA processed MCZ – Si

The GOI deterioration in NH₃ RTA processed void-rich Si wafers found by Shin [2] originates from the generation of “nano-voids” due to agglomeration of supersaturated vacancies. This effect was also studied in defect optimized MCZ Si wafers which exhibit nearly no voids at all. GOI deterioration was also found with values of typically ~2 def./cm² which were mainly “B-mode” defects found at electrical fields of 4–8 MeV cm⁻¹ (Fig. 4, left column). The non-RTA-treated wafer exhibited always a very good GOI defect density of <0.2 def./cm² indicating the absence of nearly all COPs in this MCZ substrate.

This GOI deterioration was not removable by successive CMP steps up to 3 μm as suggested by Ref. [2]. Even stock removal polishing followed by a CMP step of >15 μm showed nearly the same high GOI defect density. Only the RTA process sequence of ultrahigh temperature oxidizing RTA followed up by the NH₃ RTA step now reduced significantly the GOI defect rate (Fig. 4, right column). It has to be noted that only if the oxide film from the first oxidizing RTA step was removed by an HF step (e.g., 1.2% HF solution applied for 3–6 min) the vacancy injection by follow up NH₃ RTA step occurs. This was proved by always measuring the BMD profile after each process sequence. That the vacancy injection is suppressed via the oxide film

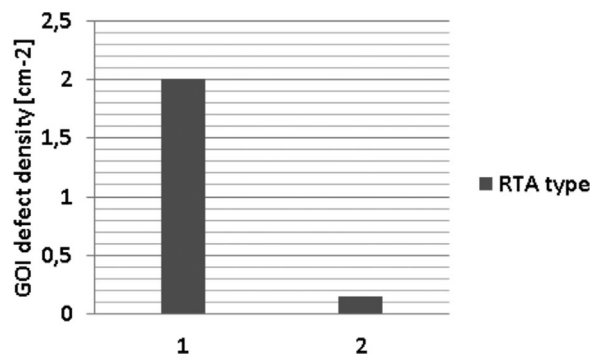


Figure 4 GOI defect densities after pure NH₃ RTA processing (left column) and after the process sequence of 1300 °C RTA in O₂ + NH₃ RTA steps (right column).

formation during an oxidizing RTA step was already demonstrated in an earlier work [22].

The root cause for the drastic GOI improvement for the process sequence 1300 °C RTA in O₂ + oxide film strip + NH₃ RTA is still not fully understood. It occurs also if only the 1300 °C oxidizing RTA step is applied (GOI defect densities <0.15 def./cm²). Possibly nano precipitates still present in the surface near region might play a role. They appear occasionally in TEM observations with sizes of ~10–15 nm. They might change their morphology/size during the vacancy injecting NH₃ RTA step. Then the oxide thinning induced by these defects during the GOI test occurs and the oxide breakdown takes place as described in Ref. [18]. The 1300 °C RTA O₂ pre-step seems to effectively reduce these defects so that the GOI defect rate is afterwards very low.

4 Conclusions In this study, the effect of basic RTA processes on void-rich N-doped CZ Si and defect optimized MCZ–Si wafers 300 mm in diameter was analyzed. At first, it was confirmed that void shrinkage and dissolution occurred down to sizes <20 nm, being the detection limit of the IRLST tool, if RTA steps at 1305 °C for 150 s in oxidizing ambient are applied. The precipitation behavior was found to be different from that claimed in Refs. [5, 7, 8]. It could be totally suppressed if a RTO process of 1310 °C for 120 s was performed and a holding step at 1200 °C during cool down for 15 s was included. If the holding step was skipped the denuded zone was large (>100 µm) and the precipitation remained small (~3E5/cm²). Shortening the holding time for the RTO step to 100 s followed by 20 s step in diluted Ar/O₂ ambient led to stronger precipitation again (~3E6/cm²).

Vacancy profiles induced by NH₃ RTA seem to be partly inhibited in “low Oi” MCZ–Si. This can be concluded by comparison of the observed onset RTA temperature with that given in Ref. [9]. The precipitation in the peak is lower and starts at ~25 °C higher temperatures. This parameter study can be helpful for a future model describing the process of vacancy injection. The stability of these vertically inhomogeneous profiles was tested at $T = 1140$ °C test cycles. The profiles completely vanished or were only slightly stabilized by a longer NH₃ exposure time. This could be understood in terms that the pure vacancy profile – as it can be found via Pt diffusion [10–15] – is not stable at these elevated temperatures because the vacancies become mobile again. Further experiments at varying holding temperatures of the stabilization test cycle (as described in Ref. [21]) would be also helpful to probe a possible Arrhenius dependency of the involved vacancy species. GOI deterioration post NH₃ RTA processing was also observed in MDZ Si wafers but the restoration mechanism was much different than given in Ref. [2]. Only high temperature RTA processing prior to the NH₃ step ensures good GOI performance. This indicates the possible

dissolution of nano-sized defects which otherwise become GOI active (as possibly their morphology is changing under the influence of excess vacancies generated by the NH₃ step).

Acknowledgements We are very thankful for Michael Boy and Christina Matzeder to perform part of the RTA experiments.

References

- [1] J. Vanhellemont, E. Kamiyama, K. Nakamura, P. Spiwak, and K. Sueoka, *J. Cryst. Growth* (2017), <https://doi.org/10.1016/j.jcrysg.2016.12.077>.
- [2] J.-W. Shin, W.-S. Lee, J.-Y. Kim, A. J. Lee, H.-B. Kang, and S.-W. Lee, *ECS Trans.* **75**(4), 77–80 (2016).
- [3] G. Kissinger, D. Kot, and W. Häckl, *ECS Trans.* **33**(11), 113 (2010).
- [4] G. Kissinger, J. Dabrowski, A. Sattler, C. Seuring, T. Müller, H. Richter, and W. von Ammon, *J. Electrochem. Soc.* **154**, H454 (2007).
- [5] H. Sudo, K. Araki, T. Aoki, and S. Maeda, *JSPS Si Symposium Proceedings*, Nov. 21–25, Kona, Hawaii, USA (2016).
- [6] M. Jacob, P. Pichler, H. Ryssel, and R. Falster, *J. Appl. Phys.* **82**, 182 (1997).
- [7] K. Araki, S. Mareda, H. Sudo, T. Aoki, and K. Izunome, *ECS Solid State Lett.* **3**(9), 114–115 (2014).
- [8] K. Araki, S. Mareda, T. Senda, H. Sudo, H. Saito, and K. Izunome, *ECS J. Solid State Sci. Technol.* **2**(3), 66–70 (2013).
- [9] J.-G. Park, G.-S. Lee, J.-S. Lee, K. Kurita, and H. Furuya, *Mater. Sci. Eng. B* **134**, (I2-3), 249–256 (2006).
- [10] V. V. Voronkov and R. Falster, *Mat. Sci. Semicond.* **5**(4–5), 387–390 (2002).
- [11] H. Zimmermann and H. Ryssel, *Appl. Phys. A* **55**, 121 (1992).
- [12] H. Zimmermann and R. Falster, *Appl. Phys. Lett.* **60**, 3250 (1992).
- [13] F. C. Frank and D. Turnbull, *Phys. Rev.* **104**, 617 (1956).
- [14] H. Zimmermann and H. Ryssel, *Appl. Phys. Lett.* **58**, 499 (1991).
- [15] G. Kissinger, D. Kot, J. Dabrowski, T. Grabolla, T. Müller, and A. Sattler, *Phys. Status Solidi (a)*, Version of record online: 26 May 2017, <https://doi.org/10.1002/pssa.2017.00236>
- [16] W. Zulehner, *Mater. Sci. Eng.* **4**, 1–10 (1989).
- [17] A. Götzberger, C. Hebling, and H.-W. Schock, *Mat. Sci. Eng. R* **40**, 1–46 (2003).
- [18] D. K. Schroder, *Semiconductor Material and Device Characterization*, 3rd edition (Wiley Interscience, New Jersey, 2006), p. 706ff.
- [19] V. V. Voronkov, *J. Cryst. Growth* **59**(3), 625–643 (1982).
- [20] V. V. Voronkov, R. Falster, T. H. Kim, S. S. Park, and T. Torack, *J. Appl. Phys.* **114**, 043520 (2013).
- [21] V. V. Voronkov, R. Falster, and P. Pichler, *Appl. Phys. Lett.* **104**, 032106 (2014).
- [22] R. Falster, M. Pagani, D. Gambaro, M. Cornara, M. Olmo, G. Ferrero, P. Pichler, and M. Jacob *Solid State Phenom.* **57–58**, 129–136 (1997).